AN ACUTE BIOASSAY STUDY OF THE EFFLUENT DISCHARGE FROM THE KIMBERLY CLARK PULP MILL TO JACKFISH BAY IN JULY, 1990 AFTER THE COMMISSIONING OF A SECONDARY TREATMENT SYSTEM

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The test fish were acclimated at the Lakehead University fisheries laboratory by Norlab Environmental Services, under the guidance of Alaister Smith.

The manuscript was reviewed by Ruth Berzel, Paul Jordan, Patrick Morash and Jim Murphy.

EXECUTIVE SUMMARY

The Kimberly Clark mill effluent is discharged to Blackbird Creek and travels approximately 15 km along the creek before entering Lake Superior at Moberly Bay and in turn out into Jackfish Bay.

In 1983, 96-hour field bioassays were undertaken by caging hatchery-reared rainbow trout at various locations in Moberly Bay and Jackfish Bay. A zone of acute fish lethality was measured throughout Moberly Bay and along the western shoreline of Jackfish Bay, 1.5km from the Blackbird Creek discharge. Depleted oxygen levels in the surface waters of the bay due to the high BOD levels in the mill effluent were the primary cause of the fish lethality.

Furthermore, composite samples of the mill effluent and Blackbird Creek were found to be lethal to rainbow trout in aerated 96-hour laboratory bioassays. Although oxygen levels in those test samples were more than adequate to substain a fish population, elevated levels of resin acids and other possible toxicants in the mill effluent produced the fish lethality observed in those tests. These results suggested that mill effluent could have been lethal to fish in Moberly Bay, even if oxygen levels in the receiving water met the provincial objectives for the protection of aquatic life.

Fish which survived the exposure were analysed for and found to contain two priority contaminants from the mill effluent, 2,4,6-trichlorophenol and pentachlorophenol.

In 1989, Kimberly Clark spent approximately $30M to install a secondary treatment system to treat all of the process effluent from the plant before its discharge to Blackbird Creek.

This study was undertaken to confirm that the acute lethality problem had been resolved by the new treatment system. All dissolved oxygen measurements undertaken in the Lake Superior receiving water met the Provincial Water Quality Objectives for the protection of aquatic life. The treatment system (and process changes) also significantly reduced the levels of chloroform, pentachlorophenol and resin acids among other contaminants. As a result of higher oxygen levels in the receiving water and lower resin acid levels in the effluent, the mill effluent was found to be non lethal to rainbow trout in laboratory bioassays while the effluent plume in Moberly and Jackfish Bays was non lethal to fathead minnows and rainbow trout in field bioassays.

INTRODUCTION

1. Background

A fish bioassay was performed during July of 1983 to assess the effects of the Kimberly Clark pulp mill effluent on Jackfish Bay (Figure 1). In that study, the surface waters of the bay were found to be lethal to rainbow trout as far as 1.5 km from the Blackbird Creek discharge and approximately 15 km down the creek from the mill site. Trace amounts of chlorophenols (contaminants commonly found in chlorine-bleached kraft mill discharges) were also measured in fish which survived the exposure (Flood et al., 1986).

Several benthic surveys have been undertaken in Jackfish Bay since 1969 (Beak, 1988), and they show that the extent of impairment had not changed much over the years. German and Pugh (1969) found that "toxic pollution" existed at the mouth of Blackbird Creek, benthal oxygen depletion persisted throughout much of Moberly Bay and the restoration of water quality in Jackfish Bay to support indigenous aquatic life did not occur until a distance of 2 km (1 1/4 miles) from the Blackbird Creek discharge. The area of impact in the bay as described by the benthos in 1970 was very similar to that observed for fish lethality in the surface waters during 1983.

In 1982, Kimberly Clark was issued a control order by the MOE, requiring the company to reduce the toxicity of its waste by October, 1986. The company could not comply due to economic hardship and therefore an extension was granted by way of a new control order, in March, 1987. The new order called for a secondary treatment system to be placed in operation by October 31st, 1989. The primary objectives of the system were to reduce the BOD of the effluent and to control the toxic components in the total mill effluent in order to meet the static bioassay toxicity requirement of the Ministry (which requires that an undiluted sample of the final effluent must not be lethal to 50% or more of the rainbow trout test fish in a 96-hour laboratory bioassay). The work was completed on schedule and aerated lab bioassays of the resultant effluent indicated that the effluent was not lethal to fish.

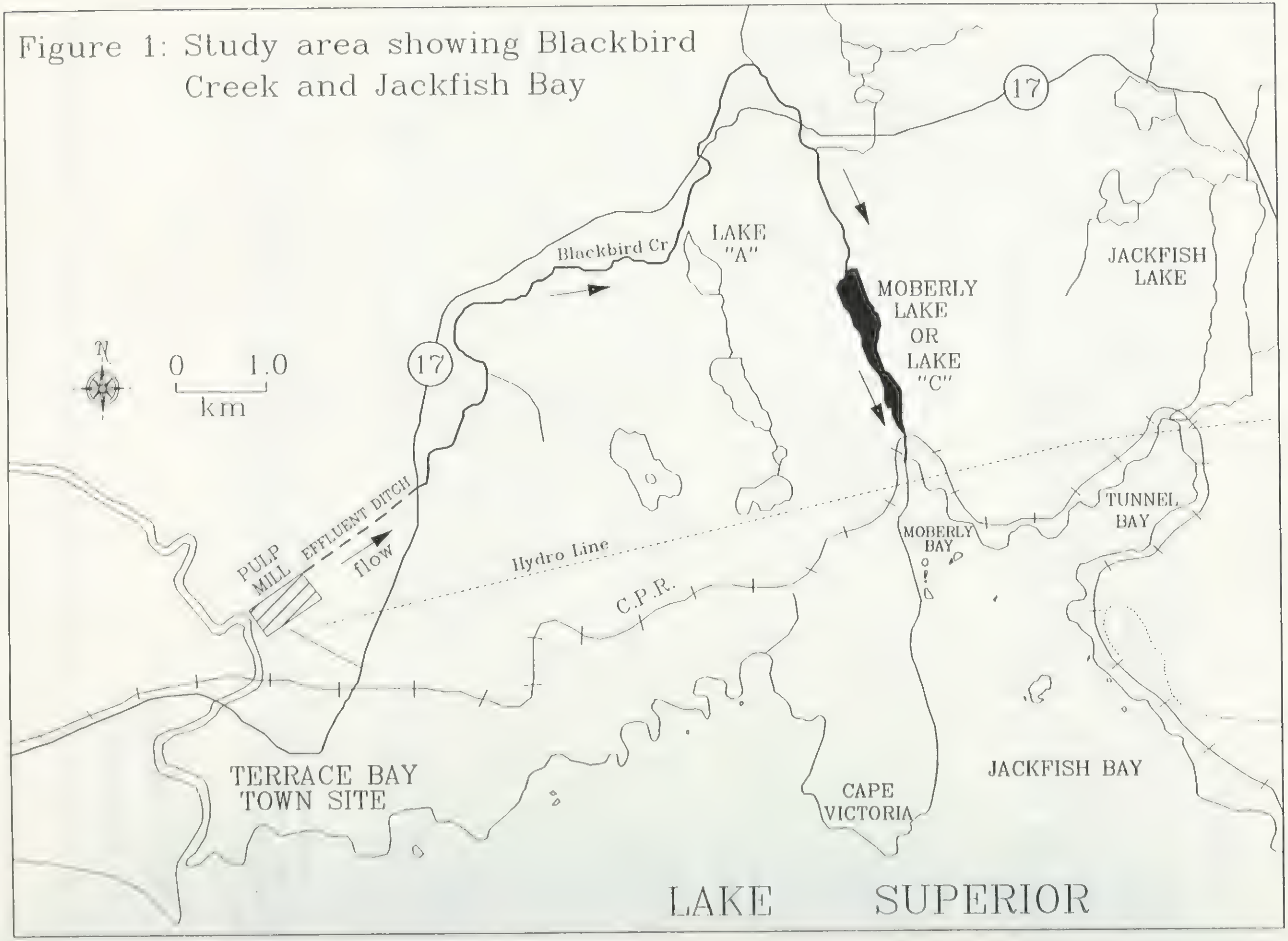
The purpose of this study was to confirm that the new treatment system would produce a non lethal effluent and acceptable dissolved oxygen conditions for the survival of fish in Jackfish Bay.

2. Mill Description

a) Production

The mill employs a chlorine-bleached kraft process to produce pulp.

Figure 1: Study area showing Blackbird Creek and Jackfish Bay



Its design capacity in 1990 was approximately 1135 tonnes of pulp per day utilizing a mix of hardwood and softwood logs and chips (1/3 and 2/3 respectively).

b) Effluent Treatment

The effluent streams in the mill are comprised of domestic sewage, plus the alkaline and acid streams. The average effluent flow from the mill in 1990 was 94.0×10^3 m^3/day (Jackfish Bay RAP Team, 1991). The alkaline and domestic sewage streams make up 80% of the effluent volume and the acid sewer accounts for the rest. The domestic stream undergoes an aerobic biological treatment before combining with the alkaline stream in the clarifer. This primary treatment system consists of two mechanical screening stages, consisting of a course bar screen and travelling screen followed by a reactor clarifier. The resultant sludge is de-watered and burned in the power boiler.

After primary treatment, the alkaline stream is mixed with the acid stream in the settling basin of the secondary treatment system to attain a neutral effluent pH. The effluent undergoes aerobic treatment while passing through three much larger cells of the secondary treatment system, where bacteria break down the effluent's organic material, with the greatest effect occurring in the first cell. The secondary treatment facility covers 34 hectares of which there is 26 hectares of pond containment area. There are 36 aerators which provide treatment during a 9-day retention time in the lagoon system (Murphy, pers. comm.).

Upon discharge from the treament system, the effluent passes along an effluent channel to Blackbird Creek. The effluent must travel approximately 15km along the creek system over a period of 1.5 to 2.0 days before it is discharged to Moberly Bay.

c) In-plant Upgrades

Since the initial fish bioassay in Jackfish Bay during 1983, many internal upgrades have been undertaken in the plant, which have helped to improve the effluent quality from the mill. Spill control systems were completed in the no. 2 mill during 1984 and the No. 1 mill in 1985. Improvements in soap recovery systems were completed in 1984 and'85. In 1985, an oxygen extraction (E.O.) stage was added to the No. 2 bleachery and the addition of new instumentation to both bleacheries resulted in a significant reduction in the use and resultant discharge of bleachery chemicals. Higher chlorine dioxide substitution was instituted in 1984 and 1990. Also in 1990, the hypochlorite stage in the bleachery was replaced by a Papricycle stage which reduced the amount of steam (fuel) required in the bleaching process. This is not an exhaustive list of internal mill changes but is included to demonstrate the type of changes instituted to reduce chemical use of production chemicals and to improve effluent quality (OMOE, file; Jackfish Bay RAP Team, 1991).

METHODOLOGY

1. Study Outline

Hatchery-reared rainbow trout and lab-reared fathead minnows were exposed in cages at various sites in Jackfish Bay in order to measure acute lethality and the bioconcentration of contaminants by fish. The exposures were undertaken over a 96-h period from July 26-30th, 1990, with fathead minnows exposed along a central transect in the bay at sites 1, 2, 4, 7, 9 and the control sites (Fig. 2), while rainbow trout were exposed at all cage locations but site 1 (due to potentially high water temperatures near their lethal threshold at that site). Fish mortality observations, water chemistry sampling and dissolved oxygen measurements were undertaken daily at each of the exposure sites. From this data, dissolved oxygen levels along the three transects in the bay (A, B & C) were determined in order to define the area of impact of the effluent (Fig. 3).

Daily 24-h composite samples of the Kimberly Clark final effluent and Blackbird Creek discharge were collected from July 24-28th, 1990 and July 26-30th, 1990, respectively. The two-day difference in the sampling schedule for the final effluent and creek discharge was undertaken in an attempt to account for the 1.5-2.0 day travel time along Blackbird Creek to Moberly Bay and hence provide an opportunity to compare lethality levels between those two sites. Those samples were submitted to the MOE Thunder Bay and Rexdale labs for chemistry analyses, and to the MOE Toxicity Unit in Rexdale for standardized 96-h bioassays with rainbow trout (Craig *et al*, 1983) and 48-h bioasssays using *Daphnia magnia* (Poirier *et al*, 1988).

Upon completion of the study, fish surviving the field exposure were sacrificed and preserved for contaminant analyses. Unfortunately, the samples were destroyed due to a freezer malfunction before the chemical analyses could be performed.

2. Field Exposure

a) Fish Stock

Rainbow trout (*Oncorhynchus mykiss*) fingerlings were obtained from Rainbow Springs hatchery, in Erin, which is designated by Agriculture Canada as a disease-free facility. The fish were shipped to Thunder Bay, air express and held at Lakehead University

Fig. 2: Fish Exposure Sites in Jackfish Bay.

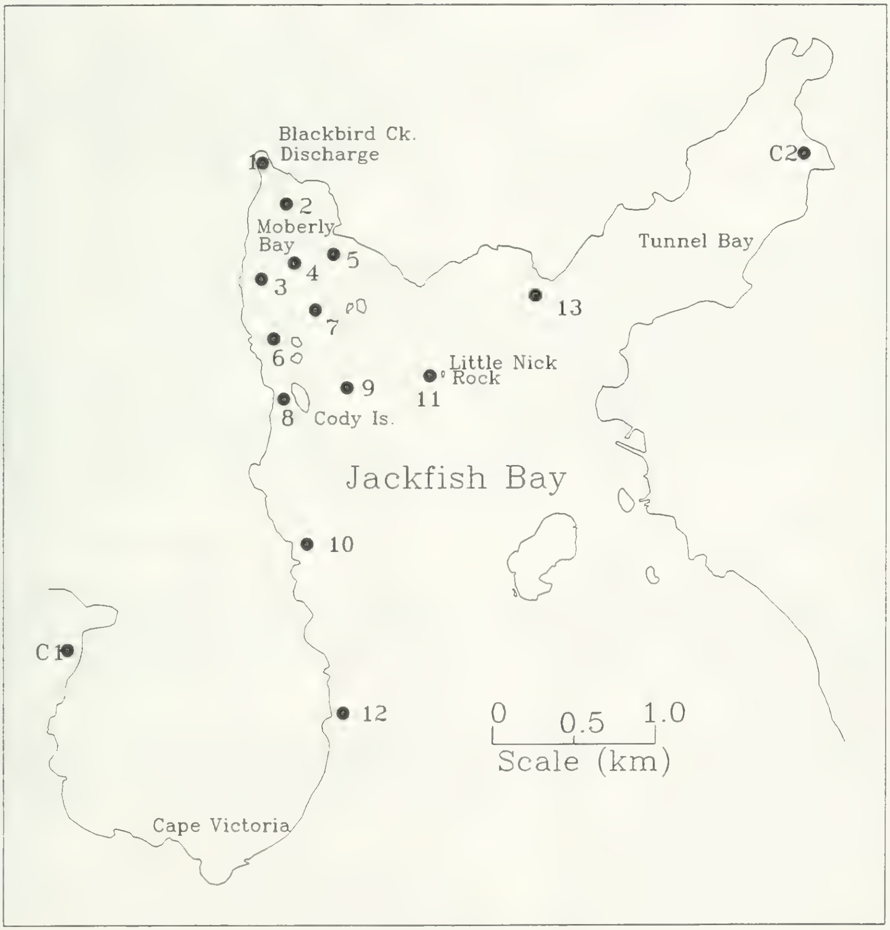
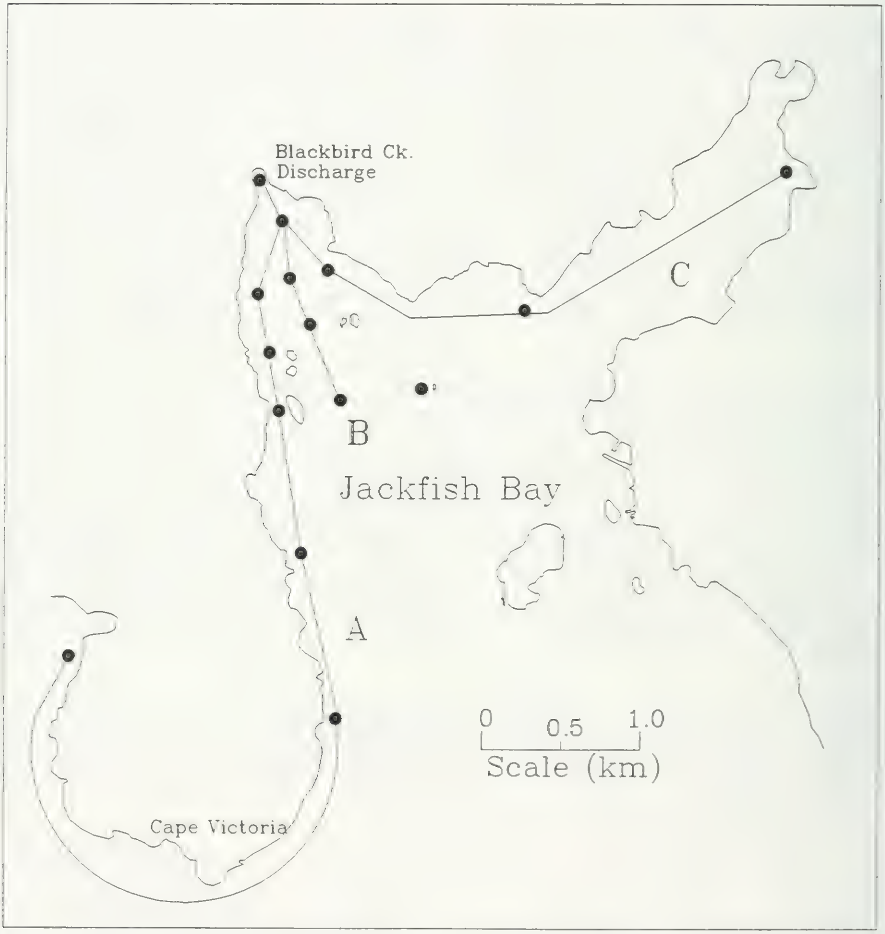


Figure 3: Dissolved Oxygen Transects in Jackfish Bay.



until required for the exposure in Jackfish Bay. They were acclimated to dechlorinated and carbon-filtered Thunder Bay tap water for a period in excess of two weeks in order for them to adjust to a soft water environment similar to that in Jackfish Bay. Water was supplied to the fish by way of a once-through delivery system providing water at a constant temperature of 16°C. The fish loading rate was in excess of 0.7 L of water/ g of fish/ day and the mean fish weight and length (+/- 2 std. dev.) was 2.4 g +/- 0.6 g and 6.5 cm +/- 0.5 cm, respectively (N=25).

Fathead minnow (Pimephales promelas) fry were also exposed at a number of sites in the study area. Those fish were obtained from a stock which was cultured by Norlab at the Lakehead University acclimation facility. They were fed a diet of frozen brine shrimp, during their acclimatiom period. The fish were acclimated to a 19°C water temperature for more than two weeks prior to use in the study. Their mean weight and length (+/- 2 std. dev.) was 0.5 g +/- 0.2 g and 4.0 cm +/- 0.5 cm, respectively.

Both sets of fish were not fed 24 hours prior to transport to the study site. On the day of transport, the fish were separated into groups of 25 and placed in food-grade polyethylene bags containing 10 L of 16°C water (for the rainbows) and 19°C (for the fatheads) from the respective water sources used in their acclimation tanks. The bags were tied off under pressure with a pure oxygen head space of 10 L and placed in 90 L "picnic" coolers, with three bags of fish per cooler. One freezer pack was placed in each cooler of rainbow trout to insure that water temperatures were maintained at 16°C.

b) Fish Cages

The cages in this study were constructed with a frame of 1.9 cm (3/4") polyvinylchloride (PVC) pipe. Their shape was triangular on the top and bottom, and had three sides, each 0.5m in length and depth. The frame supported a 0.6 cm (1/4") mesh nylon bag with a draw string closure at the top.

The cages were free-floating with the cage top at the water surface and were held in place by a rope and anchor. An empty plastic container, fluorescent orange in colour, was also tied to each cage top as a navigational marker.

3. Cage & Water Sample Locations

The cages were set out at sites similar to those used in the 1983 study (Flood et al, 1986) for comparison purposes and site 13 was added in an attempt to determine whether the plume was distinguishable in terms of both, water quality and the bioaccumulation of mill contaminants by fish, as the plume entered Tunnel Bay.

The rainbow trout were tested at all study sites in Jackfish Bay except site 1. The fathead minnows were exposed at sites 1, 2, 4, 7 and 9, along transect B (Fig. 3); plus at the two control sites.

The effluent sample location for Blackbird Creek in 1990 was approximately 75m upstream from the mouth (ie. upstream of the foam barrier) while the 1983 samples, designated as from Blackbird Creek, were collected from Moberly Bay at the closest point at which the boat could access the creek (approximately 30m out from the foam barrier). All other water sample locations were similar to those used in the 1983 study (ie. at each of the cage sites). The sample and cage sites are shown in Figure 2.

4. Procedure

The cages were put in place at the sites outlined in Figure 2, on the day before the fish were introduced and the study began. On the following day, a bag of twenty-five fish was placed in each cage and the water temperature within the bag was allowed to equilibrate to that at the exposure site (+/- 1°C) prior to releasing the fish into the cage. Observations of the fish were planned for at least once a day from that point through to the end of the test for fish mortality, loss of equilibrium, unusual swimming patterns or distinctive changes in colour relative to the controls. This protocol was followed on all days except for study day 4. Excessive fog along the north shore of Lake Superior produced conditions too dangerous for navigation to the study area on that day.

Fish were considered dead if after mild prodding, there was no visible respiration or other movement. A tally of dead fish was kept for each site and upon observation, the dead fish were removed immediately and discarded. At the end of the study, a final count of fish was made for each cage and they were set out in five composite samples of five fish for each site in the case of the rainbow trout and for the fathead minnows five composites of ten fish. The number of fish for each composite was selected in such a way as obtain samples of 10g or greater in order to carry out contaminant analyses on them. The individual composite samples were wrapped in hexane-washed foil and frozen for preservation. A pre-exposure set of fish was also sampled at the Lakehead University lab as a background check for organochlorine contaminants in the fish prior to their exposure at the study site.

The study dates, pre-study dates, study day numbers referred to in the text and number of hours of exposure on each of those days is as follows:

Date	Time	Study Day	Exposure Time
July 24	1430 h	pre-exp day 1	minus 48 h
July 25	1430 h	pre-exp day 2	minus 24 h
July 26	1430 h	1	0 h
July 28	1430 h	3	48 h
July 30	1430 h	5	96 h

5. Physical and Chemical Analyses:

a) List of Analyses

i) Industrial effluent indicators - BOD, COD, TSS, TDS, Total Residue.

ii) General water Quality - alkalinity, hardness, pH, conductivity

iii) Metals - Cu, Pb, Zn, Cd, Cr, Al, Fe, Hg.

iv) Organics - chlorophenols, chloroguaiacols, phenoxy acid herbicides, volatiles, polyaromatic hydrocarbons, resin and fatty acids.

v) Specific Contaminants - total ammonium, nitrites, nitrates, sulphides

vi) Nutrients - Na, K, Mg, Ca, Cl, sulphates.

vii) On-site analyses - temperature, conductivity and dissolved oxygen.

b) Water Sampling Program:

i) Plant Effluent

Twenty-four hour composite samples were collected daily for the seven days from July 24th - 30th, 1990, for all of the parameters listed in section 3a) above, except those in 3a vii).

ii) Blackbird Creek discharge

All parameters in 3a) were analyzed on daily grab samples from this site during the period from July 26-30th, except on July 29th, due to excessive fog.

iii) Study Site 1

All parameters in 3a) were analyzed on daily grab samples from this site except for the polyaromatic hydrocarbons (PAH's), which were analyzed on samples collected on test days 1 & 3 only.

iv) All Other Study Sites

All parameters in 3a) were analyzed on daily grab samples from these sites except for volatiles, polyaromatic hydrocarbons and sulfides . Samples were collected from July 26-30th, except day 4 (July 29th).

6. Laboratory Bioassays

Bioassays of 24-h composite samples from the Kimberly Clark final effluent and Blackbird Creek discharge were performed at the MOE Toxicity lab in Rexdale, using rainbow trout (Oncorhynchus mykiss) fry and Daphnia magna neonates.

The rainbow trout were obtained from Rainbow Springs hatchery in Erin, Ontario and their holding water temperature was raised from 10°C to 15°C at 1.0°C per day upon arrival at the Rexdale lab. After the final holding temperature was reached, the fish were acclimated to the laboratory water for 2 weeks prior to use in the bioassays and were fed Martin's granular trout chow, ad libitum, twice daily during the acclimation period.

The fish bioassays were aerated 96-h tests. In each bioassay, 10 fish were exposed per test solution and sample concentrations in each test ranged fron 10% to 100%. All dilutions were prepared using dechlorinated and carbon-filtered Toronto tap water.

During the initial 24-hour period of the test, fish mortality observations were undertaken at 1, 2, 4, and 24 hours and at least once daily at 48, 72 and 96 hours. All test solutions were kept within a temperature range of 15°C +/- 1°C and dissolved oxygen levels of all test solutions were maintained above 7.0 mg/L for the duration of the tests. None of the test solution needed pre-oxygenation prior to the initiation of the test.

The neonates (1st instar organisms) used in the Daphnia tests were less than 24-h old and are obtained from a brood stock cultured in the MOE laboratory. The Daphnia bioassays were 48-h unaerated tests performed at a water temperature of 20°C +/- 1°C. In each bioassay, 12 Daphnia were exposed per test concentration with 3 individuals per effluent tube, tested in quadruplicate. The dilution concentration range was 100%, 50%, 26%, 14% and 6% of effluent: dilution water and 100% concentration of dilution water was tested as the control solution. All dilutions were prepared using dechlorinated and carbon-filtered Toronto tap water.

Acute lethality results were presented as 96-hour or 48-hour LC50's (concentrations of the samples lethal to 50% of the test fish or Daphnia), along with their 95% (or greater) confidence limits; and as LT50's (time to 50% lethality) in the undiluted mill effluent (for the fish bioassay results only). The LC50's and their confidence limits (fiducial limits) were calculated using either Probit Analysis, Moving Average or the Spearman-Karber Method of data analyses as outlined in the "LC50 Calculation Program" developed by Charles Stephan of the USEPA. The LC50's and confidence limits for data with no partial responses were calcuated by the Binomial Theorem Method as outlined in Stephan (1977).

All test requirements and procedures met the MOE bioassay protocols which were in place at the time of this study (Craig *et al*, 1983; Poirier *et al*, 1988).

RESULTS & DISCUSSION

1. Acute Lethality

a) Laboratory Bioassays

During this study, all of the 24-h composite samples of the Kimberly Clark effluent and the Blackbird Creek discharge were not lethal to rainbow trout in 96-h laboratory bioassays, and therefore, the 96-hour LC50 for those samples would be greater than 100%. As a result, the mill effluent was considered to have met all of the conditions of the 1987 control order involving rainbow trout lethality, was in compliance with the proposed toxicity criteria for the MISA regulation of industrial discharges and met the acute lethality requirement of the new federal regulation for pulp and paper mill wastes. Similar results were measured in rainbow trout bioassays of the Kimberly Clark final effluent, sampled monthly throughout the MISA study of 1990 (OMOE, 1992a & 1992b).

A portion of the test organisms died in Daphnia bioassays of the Kimberly Clark final effluent and Blackbird Creek discharge samples collected on July 26th, 1990. However, the mortality occurred at insufficient levels to calculate an LC50 (ie. less than 50% of the Daphnia died in the full strength effluent samples) and therefore the LC50 of both tests were reported as > 100% effluent. All other samples, which were also duplicates of those tested in the fish bioassays, had < 10% mortality in each test with most being non lethal (Appendices A & B).

b) Field Observations

There was no fish mortality observed at cage sites in Moberly Bay or Jackfish Bay over a 96-h period from July 26-30th, 1992.

Furthermore, approximately 20-25 suckers (Catostomus sp.) broke water in order to evade our boat in the uppermost reaches of Moberly Bay on several days during the study. It is believed that those fish were foraging in the bay.

There was no fish activity observed in Moberly Bay during the 1983 study. A survey undertaken in the area during 1986 found only one fish, a longnose sucker (Catostomus catostomus) in Moberly Bay, while numerous fish consisting of 16 different species were caught in various parts of Jackfish Bay (Hamilton, 1987). The combination of recent and past observations of fish activity in the area, suggest that the water quality has improved in Moberly Bay, to the point that at least some fish no longer avoid the area.

2. Dissolved Oxygen (DO)

Dissolved oxygen in Moberly Bay (approximately 50m from Blackbird Creek discharge) ranged from 6.8-7.3 mg/L in daily readings during the period from July 26-30th, 1990 (Table 1). All other sites had DO levels of 8.0 mg/L or higher throughout the study while levels at the C-1 control site ranged from 10.8-11.3 mg/L. In terms of the percentage saturation of oxygen, the lowest DO measured at an exposure site during the study was 73%.

Therefore, all of the DO levels measured in the surface waters of the study area met the Provincial Water Quality Objective (PWQO) for the protection of aquatic life with DO levels greater than 4.0 mg/L (47% saturation) for warm water biota and 5.0 mg/L (57% saturation) for cold water biota.

a) Comparison of Dissolved Oxygen in Jackfish Bay in 1990 vs 1983.

During worst case conditions in 1983, the lowest DO levels occurred along the western shore of Jackfish Bay (transect A) while progressively greater values were present along the central and eastern transects, respectively (Fig 3). The PWQO for dissolved oxygen was not met in 24% of the measurements in Jackfish Bay during the 1983 study (Table 2). On two of four study days, an exceedance of the PWQO occurred along the western shoreline of Jackfish Bay as far as 1500m from the Blackbird Creek discharge (site #8) and occurred over a 1000m distance along the central transect on one occasion (site #7).

There was a dramatic improvement in worst case conditions for dissolved oxygen in the surface waters of Jackfish Bay in 1990 versus 1983 (Table 3, Fig. 4 & 5). Daily measurements of DO at the Blackbird Creek discharge ranged from 4.2-5.2 mg/L during July 10-14, 1983 versus 6.8-7.3 mg/L from July 26-30, 1990. The lowest DO measured during the 1983 study was 27% saturation

Table 1: Dissolved oxygen levels at the fish exposure sites in Jackfish Bay, July 26–30, 1990.

Site No.	Desciption	Dissolved Oxygen Levels (mg/L) on Day1	Day2	Day3	Day4	Day5
1	Blackbird Creek discharge	6.8	6.8	7.3	–	7.2
2	0.3 km out, centre	8.5	10.2	8.5	–	9.4
3	0.75 km out, westshore	8.6	8.9	8.6	–	9.5
4	0.75 km out, centre	8.7	10.0	9.6	–	9.5
5	0.75 km out, northshore	9.4	10.4	10.0	–	9.2
6	1.0 km out, westshore	8.0	9.0	9.5	–	9.7
7	1.0 km out, centre	9.5	10.0	10.0	–	9.7
8	Cody Island, westshore	8.0	8.6	9.8	–	9.8
9	Cody Island, centre	9.5	10.5	10.0	–	10.1
10	2.4 km out, westshore	9.3	9.7	10.6	–	10.6
11	Little Nick Rock	9.8	10.5	10.3	–	10.5
12	3.5 km out, westshore	9.4	9.8	10.8	–	10.7
13	mouth of Tunnel Bay	9.7	10.5	10.5	–	11.9
C1	Control 1, Victoria Bay	10.8	10.9	11.1	–	11.3
C2	Control 2, Tunnel Bay	9.7	10.6	10.5	–	11.4

Note: No observations were taken on Day 4(July 29), due to poor weather conditions for navigation.

Table 2: Dissolved oxygen levels at the fish exposure sites in Jackfish Bay, July 10–14, 1983.

No.	Site Desciption	% Saturation of Dissolved Oxygen on Day1	Day2	Day3	Day4	Day5
1	Blackbird Creek discharge	62	–	60	49*	48*
2	0.3 km out, centre	42*	–	30**	75	37**
3	0.75 km out, westshore	69	–	27**	77	46**
4	0.75 km out, centre	64	–	35**	81	44**
5	0.75 km out, northshore	85	–	76	82	96
6	1.0 km out, westshore	71	–	33**	76	41**
7	1.0 km out, centre	96	–	83	84	47*
8	Cody Island, westshore	66	–	28**	94	44**
9	Cody Island, centre	87	–	66	88	91
10	2.4 km out, westshore	89	–	99	88	95
11	Little Nick Rock	95	–	97	90	97
12	3.5 km out, westshore	96	–	102	95	104
13	mouth of Tunnel Bay	–	–	–	–	–
C1	Control 1, Victoria Bay	107	–	–	91	95
C2	Control 2, Tunnel Bay	103	–	98	–	99

Note: "–" indicates no measurement taken.

No observations were taken on Day 2(July 11), due to poor weather conditions for navigation.

* denotes dissolved oxygen conditions which did not meet the minimum Provincial Water Quality Objective for the protection of cold–water biota.

** denotes dissolved oxygen conditions which did not meet the minimum Provincial Water Quality Objective for the protection of warm or cold–water biota.

Table 3: A comparision of dissolved oxygen levels at the fish exposure sites in Jackfish Bay during the period from July 26-30, 1990 vs. July 10-14, 1983.

Sites		% Saturation of Dissolved Oxygen at the Exposure Sites with values set out from Low to High							
No.	Description	Lowest Values						Highest Values	
		1990	1983	1990	1983	1990	1983	1990	1983
1	Blackbird Creek discharge	73	(48*)	75	(49*)	79	(60)	82	(62)
2	0.3 km out, centre	84	(30**)	89	(37**)	95	(42*)	101	(75)
3	0.75 km out, westshore	85	(27**)	91	(46**)	92	(69)	97	(77)
4	0.75 km out, centre	86	(35**)	98	(44**)	99	(64)	99	(81)
5	0.75 km out, northshore	91	(76)	94	(82)	103	(85)	103	(96)
6	1.0 km out, westshore	81	(33**)	92	(41**)	98	(71)	98	(76)
7	1.0 km out, centre	92	(47*)	98	(83)	99	(84)	102	(96)
8	Cody Island, westshore	81	(28**)	89	(44**)	99	(66)	101	(94)
9	Cody Island, centre	92	(66)	99	(87)	102	(88)	104	(91)
10	2.4 km out, westshore	92	(88)	98	(89)	105	(95)	106	(99)
11	Little Nick Rock	95	(90)	102	(95)	103	(97)	104	(97)
12	3.5 km out, westshore	91	(95)	99	(96)	105	(102)	106	(104)
13	mouth of Tunnel Bay	94	(-)	103	(-)	105	(-)	107	(-)
C1	Control 1, Victoria Bay	98	(91)	102	(95)	106	(-)	107	(107)
C2	Control 2, Tunnel Bay	94	(98)	105	(99)	106	(103)	109	(-)

Note: The 1990 data is presented with the 1983 data in brackets.

"-" indicates no measurement taken.

There were only four measurements recorded because samples could not be measured on one day in both studies due to extreme fog.

* designates a value which does not meet the PWQO to protect a cold-water fishery.

** designates a value which does not meet the PWQO to protect a warm or or cold-water fishery.

Fig. 4: Minimum Dissolved Oxygen Levels measured along transects (A,B & C) in Jackfish Bay during the 1983 Study.

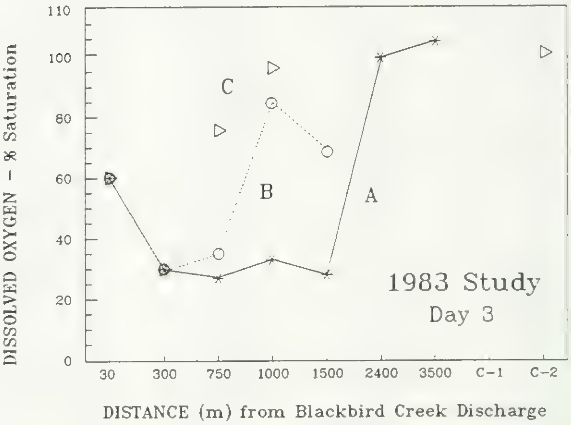
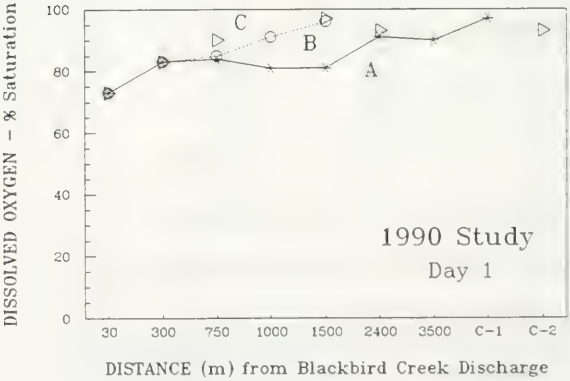


Fig. 5: Minimum Dissolved Oxygen Levels measured along transects (A,B & C) in Jackfish Bay during the 1990 Study.



(2.6 mg/L at site 3) as compared to 73% saturation (6.8 mg/L at site 1) during the 1990 study. Under worst case conditions in 1983, a DO sag to levels of less than those measured at the Blackbird Creek discharge occurred out in the bay. A similar residual effect was not observed during worst case conditions in 1990 (Fig. 6). These results suggest that full and adequate treatment of the effluent in regard to BOD and resultant dissolved oxygen levels had occurred prior to discharge into Jackfish Bay.

3. Resin & Fatty Acids (R & F A)

Prior to the commissioning of a secondary treatment facility at the Kimberly Clark, Terrace Bay mill, resin & fatty acids were found in the mill effluent, Moberly Bay and Jackfish Bay. In 1983, 7 of the 8 resin acids species were measured in the mill's final effluent and Moberly Bay with only neoabietic acid not found. Abietic (AA) and dehydroabietic acid (DHA) were present at the highest levels with concentrations in the effluent ranging from 278 - 1300 ug/L and 236 -760 ug/L, respectivily (N=4). In Moberly Bay, AA and DHA levels ranged from 482 - 808 ug/L and 392 - 596 ug/L, respectively (N=3).

Levopimaric acid was also measured at substantial levels during the 1983 study, with maximum values of 560 ug/L in the effluent and 264 ug/L in Moberly Bay.

Sherman (1991) found high abietic, dehydroabietic and levopimaric acid levels in the mill effluent during 1987 and 1988. A comparision of the resin acids concentrations in each the studies undertaken in 1983, 1987 and 1988 with the results of this study and the MISA studies (MISA, 1991a; MISA, 1991b) in 1990 demonstrates a decrease in levels over time (Table 4). A summary of the approximate differences is as follows:

for Abietic Acid, levels in 1983 > 1988 > 1987 > 1990 "M" = 1990

for Dehydroabietic Acid, levels in 1983 = 1988 > 1987 > 1990 "M" = 1990.

for Levopimaric Acid, levels in 1983 > 1988 > 1987 > 1990 "M" = 1990,

where " = " signifies values which are similar to each other.
" M " signifies values for the 1990 MISA studies.

The most dramatic decrease in resin acids discharged from the mill occurred in this study. Resin acids were not detected in 5 mill effluent samples collected once daily from July 24-28, 1990. Similar results occurred in three previous samples of effluent collected periodically since October of 1989. All of these results occurred after the commissioning of the secondary effluent system at the mill.

Fig. 6: Worst Case Dissolved Oxygen Conditions in Jackfish Bay during the 1983 and 1990 Studies.

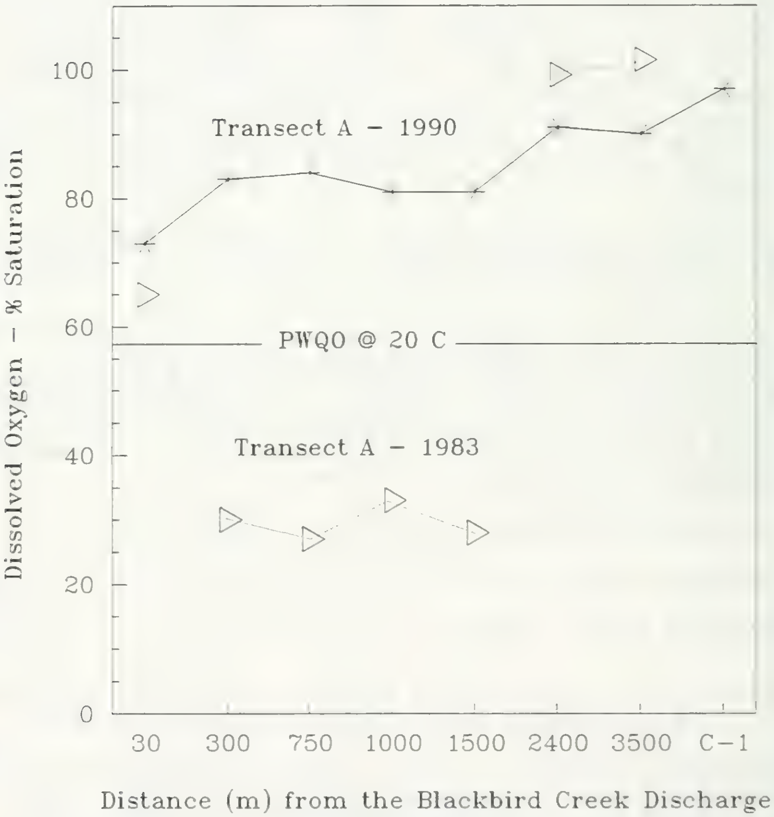


Table 4: Abietic acid, dehydroabietic acid and levopimaric acid levels (μg/L) in the Kimberly Clark mill effluent during studies from 1983 through to 1990.

I. Abietic Acid

Year of Study:	1983	1987	1988	1990	1990
Report:	(Flood et al, 1986)	(Sherman, 1990)	(Sherman, 1990)	(MISA, 1991)	(Flood et al, 1986)
Mean (S.D.)	684 (458)	45 (69)	346 (566)	25*	ND
Median	580	10	180	ND	ND
Range	278 – 1300	NA	NA	ND	ND
% > detection (N=)	100% (4)	55% (20)	100% (17)	50% (12)	0 (5)

II. Dehydroabietic Acid

Year of Study:	1983	1987	1988	1990	1990
Report:	(Flood et al, 1986)	(Sherman, 1990)	(Sherman, 1990)	(MISA, 1991)	(Flood et al, 1986)
Mean (S.D.)	463 (231)	120 (147)	491 (728)	10*	ND
Median	285	45	255	ND	ND
Range	236 – 760	NA	NA	ND – 130	ND
% > detection (N=)	100% (4)	75% (20)	100% (17)	38% (156)	0 (5)

III. Levopimaric Acid

Year of Study:	1983	1987	1988	1990	1990
Report:	(Flood et al, 1986)	(Sherman, 1990)	(Sherman, 1990)	(MISA, 1991)	(Flood et al, 1986)
Mean (S.D.)	304 (186)	13 (6)	95 (206)	ND*	ND
Median	266	<10	30	ND	ND
Range	125 – 560	NA	NA	ND	ND
% > detection (N=)	100% (4)	25% (20)	71% (17)	0 (12)	0 (5)

Note: NA denotes "not available".

ND denotes "not detectable".

Detection levels = 10 μg/L unless otherwise noted.

* denotes average value (see Table 5 footnotes for further information).

In the identification of toxic constituents of kraft mill effluents, Leach and Thakore (1973,1977) found seven resin acids to be the "major toxic factors" in Canadian softwood kraft mills, with as much as 80% of the toxicity caused by their resin acid soaps. Furthermore, acute lethality from resin acids is due to the additive effects of the individual resin acid found in solution (Taylor, 1988). In the 1983 study, the acute fish lethality measured in the laboratory bioassays of the Kimberly Clark and Blackbird Creek final effluents was for the most part accounted for by the additive effect of the resin acids in those samples (Flood et al, 1986). In 1990, resin acids were absent from the Kimberly Clark final effluent and as expected the effluent was not lethal to rainbow trout in laboratory bioassays.

In 1983, concentrations of resin acids in the outer portion of Moberly Bay decreased dramatically from levels measured near the Blackbird Creek discharge. Nevertheless, the PWQO for resin acids of 8 ug/L for dehydroabietic acid (DHA) and 25 ug/L for total resin acids (TRA) (at a pH of 7.0) were exceeded at 5 of the 6 Moberly Bay sample sites in the case of TRA and at all 6 sites for DHA. Beyond Moberly Bay, the PWQO's for resin acids were exceeded at only one of 5 sites. The resin acids measured in Jackfish Bay could not in themselves account for the fish lethality at the exposure sites during the 1983 study. Low dissolved oxygen in the receiving water was the principal reason for the acute fish lethality at those sites (Flood et al, 1986).

Sherman found that dehydroabietic acid was entering Moberly Bay at levels of 200 - 300 ug/L on July 1st, 1987 and July, 24th, 1988. In turn, DHA levels in Moberly Bay exceeded the PWQO during the 1987 and 1988 sample runs (Jackfish Bay RAP team, 1991); although, as was the case in 1983, resin acid concentrations dropped dramatically beyond the initial narrow confinement of the bay.

During the 1990 study, resin acids were not detected in daily samples collected from Moberly or Jackfish Bay over the 5-day period from July 26-30, 1990. The only resin or fatty acid consistently measured in the effluent and Moberly Bay was palmitic acid, but only in trace amounts (maximum 26 ug/L).

The 1990 data shows a dramatic change in resin acid levels in the Kimberly Clark final effluent, and consequently in Moberly Bay, after the secondary treatment system came on line. Resin acids were eliminated from the effluent and hence all samples which were collected from Moberly Bay and Jackfish Bay in 1990. This is the first evidence of the mill's receiving water being in compliance with the PWQO for resin acids on a consistent basis since RA sampling began at this site in 1983. This is not surprising for it is an accepted fact that a well-operated secondary treatment plant will readily degrade resin and fatty acids (Bonsor et al, 1988) with an estimate of 90% disappearance of resin acids and about 70% for fatty acids (McLeay, 1987).

The low resin acid levels in this study were confirmed by the MISA results throughout 1990 (Table 4), although the MISA results demonstrated a less dramatic decrease in values (MISA, 1991a & 1991b).

There are currently no PWQOs for aromatic or fatty acids since they are expected to have little or no impact on the biota under levels found in the environment due to natural or man-made sources.

4. Volatile Organohalides

The only organohalide detected in the mill effluent or receiving water was chloroform. A list of compounds in the analysis and their detection levels are presented in Appendix C.

The Great Lakes Water Quality Agreement identified chloroform as a hazardous substance (IJC, 1978), which is a known animal carcinogen (B.C. Research 1979; USDHHS, 1981). Currently, there are no provincial or federal guidelines for chloroform.

In August of 1982, a sample of the Kimberly Clark final effluent had a chloroform level of 613 ug/L (Cherwinsky & Murray, 1986). In samples collected in July of 1987 (N=16) and 1988 (N=17), Sherman (1991) found median chloroform levels of 508 and 746 ug/L respectivily in the final effluent, while median levels of 85 and 80 ug/L respectively, were measured in the Blackbird Creek discharge.

In this study, chloroform levels ranged from 4.0 - 6.4 ug/L in samples of the mill effluent collected from July 24-28th, 1990 (N=5) and from 0.9 -1.0 ug/L (N=4) at the Blackbird Creek discharge from July 26-30th, 1990 (Appendix C). No samples were collected in the bay but levels there would probably have been non detectable, based on the levels found in the creek.

Based on the most recent values for chloroform found in the Kimberly Clark final effluent (4.0 - 6.4 ug/L), relative to the median values of 508 and 746 ug/L found by Sherman (1991) in 1987 and 1988, it appears that the secondary treatment plant and/or process changes in the mill significantly reduced the levels of chloroform in the final effluent.

Evidence of reductions in chloroform levels are confirmed in the 1990 MISA data for the Kimberly Clark effluent. Samples collected monthly throughout the year had an average chloroform concentration of 12 ug/L and a range of from 4.4 to 24.3 ug/L, which is an order of magnitude less than levels found in effluent by Sherman (1990) during 1987 and 1988.

The chloroform concentrations in this study were significantly less than the USEPA criteria required for the protection of aquatic life (USEPA, 1980).

5. Chlorophenols

Chlorophenols are commonly found in bleached and semi-bleached kraft mill effluents. They bioconcentrate readily in fish and pentachlorophenol is considered to be deleterious to the environment by the IJC (1981) and a priority substance by Environment Canada.

There were two chlorophenols species found at significant levels in the final mill effluent and Jackfish Bay during our 1983 study. They were the 2,4,6-trichlorophenol and pentachlorophenol species, and they occurred in the effluent at levels ranging from 7800 - 16200 ng/L and 820 - 2250 ng/L, respectively (N=4). Sherman also found high concentrations of both of those compounds during surveys in 1987 and 1988 (Table 5). In the MISA studies (1991a, 1991b) undertaken throughout 1990, the 2,4,6-trichlorophenol levels were similar to those in 1987 and 1988, while pentachlorophenols were much less prevalent in 1990 (Table 5).

During our 1990 study, 2,4,6 - TCP was detected in 2 of 4 effluent samples and the maximum concentration was found to be 90 ng/L (Appendix D). In the same set of samples, pentachlorophenol was detected in only 1 of 4 measurements and that value was 80 ng/L. These concentrations for 2,4,6-trichlorophenol were 2 orders of magnitude lower than the 1983, '87, '88 and the MISA 1990 levels. For pentachlorophenol, concentrations in this study were two orders of magnitude less than those in 1983 and 1987, one order less than those of 1988 and for the most part, similar to those of the 1990 MISA study (Table 5).

These results suggest that there was a decrease in pentachlorophenol levels in the final effluent between 1988 and 1990, either due to changes in the mill's bleaching process, or possibly due to the the new secondary treatment system brought on-line in the summer of 1989.

When the MISA audit samples are compared amongst themselves, 2,4,6-trichlorophenol and pentachlorophenol levels in samples collected in the second half of the year appeared to be less than values in the first 6-month period of 1990 (Table below).

	Average Levels (ng/L)	Range (ng/L)	% with Detectable Levels
2,4,6 - TCP			
1st half of yr.	6750	1800 - 8800	100
2nd half of yr.	2450	nd - 5600	50
Pentachlorophenol			
1st half of yr.	170	nd - 1000	17
2nd half of yr.	<50	nd	0

During 1990, improvements were made in the bleach plant operatiom

Table 5: 2,4,6-Trichlorophenol and Pentachlorophenol levels (ng/L) in the Kimberly Clark mill effluent during studies from 1983 through to 1990.

I. 2,4,6 – Trichlorophenol

Year of Study: Report:	1983 (Flood et al, 1986)	1987 (Sherman, 1990)	1988 (Sherman, 1990)	1990 (MISA, 1991)	1990 (Flood et al, 1986)
Mean (S.D.)	11,650(3472)	8,747(6916)	4,263(2963)	6,750*	63(29)
Median	11,300	8,310	5,113	–	68
Range	7,800–16,200	ND–21,000	ND–9,000	ND–8,800	ND–90
% > detection (N=)	100% (4)	94% (17)	75% (16)	75% (12)	75% (4)

II. Pentachlorophenol

Year of Study: Report:	1983 (Flood et al, 1986)	1987 (Sherman, 1990)	1988 (Sherman, 1990)	1990 (MISA, 1991)	1990 (Flood et al, 1986)
Mean (S.D.)	1,260(671)	2021(1671)	434(254)	83*	<50
Median	985	1500	410	ND	ND
Range	820–2250	ND–5,250	ND–1100	ND–1000	ND–80
% > detection (N=)	100% (4)	94% (17)	76% (17)	8% (12)	25% (4)

Note: NA denotes ″not available″

ND denotes ″not detectable″

Detection levels = 50 ng/L unless otherwise noted.

* In the MISA (1991) report, mean values were calculated by treating values which were less than the detection level as zero.

In the Flood et al (1986) report, the mean and standard deviations were calculated by giving values which were less than the detection level an arbitrary value of ½ the detection value.

of the mill which included: higher chlorine dioxide substitution, the hypochlorite stage replacement with a Papricycle stage and the incorporation of a new control system. These changes may account for the differences in chlorophenol levels during the MISA study.

The low chlorophenol concentrations in the final effluent during the 1990 fish exposure translated into dramatic reductions of CP concentrations found in Jackfish Bay (Appendix E). In 1983, detectable levels of CP's were found throughout Moberly Bay (Flood et al, 1986), with levels ranging from 100 - 5500 ng/L for pentachlorophenol and from non detectable to 5800 ng/L for 2,4,6 - trichlorophenol. Furthermore, they were measured out into Jackfish Bay as far away as 1.5 km from the Blackbird Creek discharge for pentachlorophenol and 3.5 km for 2,4,6 - trichlorophenol. In 1990, only a single value for both pentachlorophenol and 2,4,6 - trichlorophenol was detected in four daily samples from 13 sites in Jackfish Bay; and they occurred at sites near the mouth of Tunnel Bay (340 ng/L for PCP) and out by Cody Island (90 ng/L for 2,4,6 - TCP).

Two tetrachlorophenol species were found in 1 of 4 effluent samples during the 1990 study, while only 2,3,4,5-tetrachlorophenol was measured at two adjacent sites in Jackfish Bay during one of the four sampling days. Neither level exceeded the tetraCP PWQO of 1000 ng/L in those samples.

The PWQO for 2,4,6-Trichlorophenol of 18,000 ng/L was not exceeded in any samples from Moberly or Jackfish Bay sites during the 1983, '87, '88 or '90 studies. The PWQO for pentachlorophenol of 500 ng/L has not been exceeded since the 1983 study.

6. Metals

Cadmium at the control sites equaled or exceeded its PWQO in 7 of 8 samples. Therefore as expected, cadmium levels at all exposure sites exceeded the PWQO, although those were still less than the highest control level in all but one case (Table 6). Therefore, it does not appear that the mill effluent contributed significant concentrations of cadmium to the environment, but is likely due to the geochemistry of the bedrock in that area. A comparision of metal concentrations in the mill effluent with those from the Blackbird Creek discharge is shown in Figure 7.

Copper concentrations did not exceed the PWQO (5.0 ug/L) in Moberly Bay but did exceed the objective in 1 of 4 Blackbird Creek discharge samples with a level of 11 ug/L (Table 7). Aluminum, iron, chromium and zinc levels in water samples from Blackbird Creek and site 1 in Moberly Bay exceeded their respective PWQOs. Beyond site 1, the iron and chromium criteria were met in all cases, zinc exceedances were confined to Moberly Bay while the aluminum criteria was surpassed in Moberly Bay and into Jackfish

Table 6: Metal concentrations measured at the fish exposure sites in Jackfish Bay during the period from July 26–30, 1990.

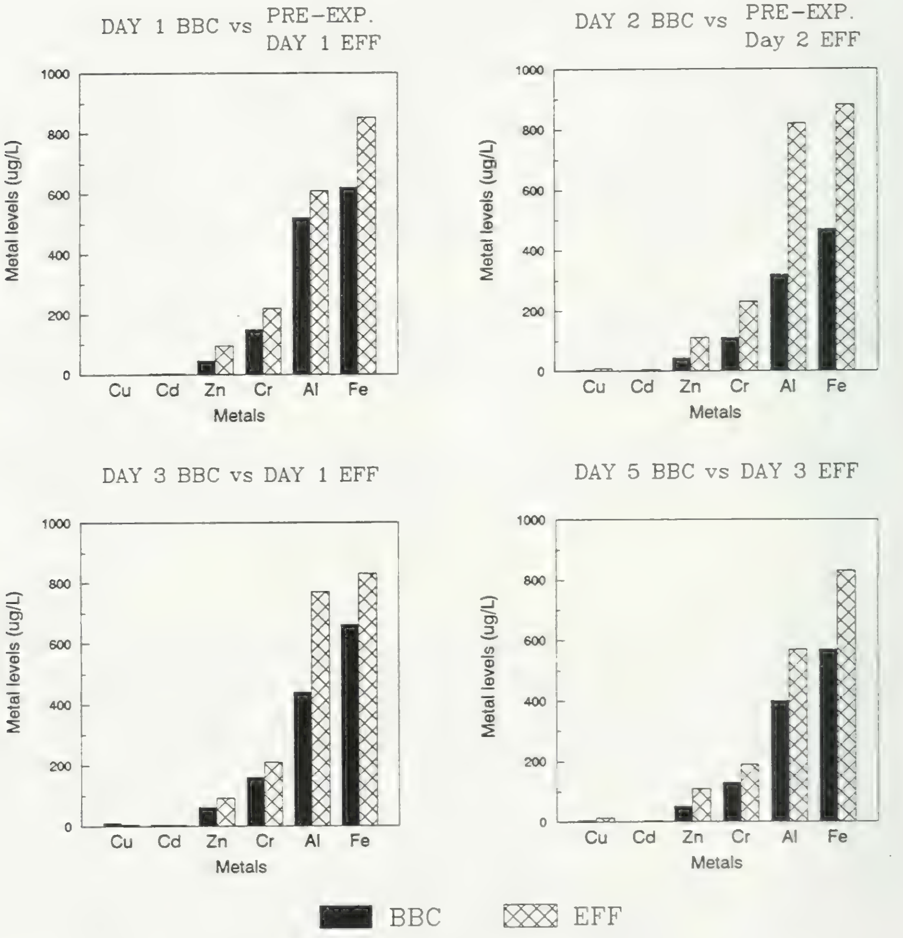
DAY No.	METAL	Metal Concentrations (µg/L) at sites															PWQO
		C1	C2	1	2	3	4	5	6	7	8	9	10	11	12	13	
DAY1	Copper	–	–	4.5	–	–	–	–	1.3	1.1	0.6	–	–	–	–	–	5
	Lead	–	–	–	–	–	–	–	7.0	3.0	–	4.5	2.5	3.5	4.0	–	20-25
	Zinc	–	–	45 *	8.5	9.5	6.4	3.0	43	4.4	10	6.2	3.4	1.7	6.6	1.4	30
	Iron	13	25	570 *	140	160	120	60	150	41	140	38	50	22	39	22	300
	Aluminum	15	21	410 *	97 *	100 *	82 *	45	96 *	33	99 *	26	36	20	29	18	75
	Cadmium	0.6 *	–	0.5 *	0.3 *	0.3 *	–	–	0.7 *	0.3 *	0.4 *	0.3 *	0.3 *	0.3 *	0.4 *	0.3 *	0.2
	Chromium	–	–	140 *	29 *	33 *	23 *	5.9 *	33 *	5.5 *	31 *	5.5 *	8.0 *	1.5	5.5 *	1.5	5
DAY2	Copper	–	–	2.2	–	–	–	1.0	1.5	0.6	1.0	–	–	–	–	–	5
	Lead	2.5	–	2.0	2.0	2.5	–	–	–	–	–	–	–	–	–	–	20-25
	Zinc	2.1	2.8	38 *	4.1	11	4.8	2.2	8.9	2.6	10	1.2	3.4	–	2.6	–	30
	Iron	9.0	24	470 *	52	140	58	44	120	43	140	27	55	23	49	25	300
	Aluminum	6.0	24	330 *	42	96 *	42	31	84 *	35	94 *	21	37	18	35	20	75
	Cadmium	0.3 *	0.3 *	0.4 *	–	0.4 *	0.4 *	–	–	–	–	–	–	–	–	–	0.2
	Chromium	–	1.2	110 *	9.0	32 *	9.5 *	6.5 *	26 *	6.5 *	30 *	2.5	9.5 *	–	7.5 *	–	5
DAY3	Copper	0.9	0.9	4.3	1.5	2.0	1.2	1.0	1.8	1.0	1.3	1.3	0.8	0.8	0.8	0.7	5
	Lead	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	20-25
	Zinc	–	–	48 *	20	70	14	9.1	6.2	2.1	5.1	1.5	1.1	–	–	–	30
	Iron	11	28	610 *	140	220	99	84	100	45	76	44	25	25	10	20	300
	Aluminum	9.0	29	410 *	95 *	140 *	66	61	70	33	53	30	16	16	7.5	20	75
	Cadmium	0.3 *	0.3 *	0.3 *	0.4 *	0.5 *	0.4 *	0.3 *	0.4 *	0.3 *	0.4 *	0.3 *	0.3 *	0.3 *	0.3 *	0.3 *	0.2
	Chromium	–	–	150 *	29 *	50 *	20 *	15 *	22 *	7.4 *	15 *	8.6 *	3.8	4.5	–	1.0	5
DAY4	NO SAMPLES COLLECTED																
DAY5	Copper	0.8	1.2	2.9	1.5	1.4	1.4	1.5	1.4	1.0	0.9	1.1	1.1	1.0	0.7	0.7	5
	Lead	2.0	2.0	–	–	–	–	–	–	–	–	–	–	–	–	–	20-25
	Zinc	1.0	3.0	51 *	8.1	6.6	7.2	9.8	5.1	3.2	2.9	4.4	1.4	1.8	1.5	1.3	30
	Iron	9.0	19	640 *	120	97	110	130	77	52	49	70	27	34	26	18	300
	Aluminum	10	16	440 *	95 *	78 *	85 *	100 *	63	44	43	60	31	35	28	21	75
	Cadmium	0.2	0.2	–	0.3 *	0.4 *	0.4 *	0.4 *	0.4 *	0.4 *	0.3 *	0.4 *	0.5 *	0.4 *	0.3 *	0.5 *	0.2
	Chromium	1.0	1.0	140 *	23 *	19 *	21 *	29 *	15 *	9.0 *	8.5 *	13 *	3.5	4.5	3.0	1.5	5

Note: All measurements were undertaken on unfiltered samples.

"–" denotes below the detection level

* exceeds PWQO.

Figure 7: A comparison of metal levels in the final effluent (EFF) of the Kimberly Clark mill with levels at the Blackbird Creek discharge (BBC) during the period from July 24th (Pre-exp Day1), 1990 to July 30th (Day 5), 1990.



Note: The travel time of the mill effluent along Blackbird Creek to its final discharge is 1.5-2.0 days. To compare metal levels at the creek discharge relative to final effluent values, the BBC samples are presented alongside the results of effluent samples collected two days previously.

Table 7: Metal levels (µg/L) in the final effluent (EFF) from the Kimberly Clark mill and the Blackbird Creek discharge (BBC) during the period from July 24, 1990. (Pre–exp Day 1) to July 30, 1990 (Day 5).

METAL	PRE–EXP DAY 1		PRE–EXP DAY 2		DAY 1		DAY 2		DAY 3		DAY 4		DAY 5		PWQO
	EFF	BBC	EFF	BBC	EFF	BBC	EFF	BBC	EFF	BBC	EFF	BBC	EFF	BBC	
Copper	–	NS	7.7	NS	5.0	–	4.5	2.5	14	11	NS	NS	NS	4.8	5
Lead	–	NS	–	NS	–	–	5.0	4.0	–	–	NS	NS	NS	–	25*
Zinc	95	NS	110	NS	92	45	70	43	110	61	NS	NS	NS	52	30
Iron	850	NS	880	NS	830	620	610	470	830	660	NS	NS	NS	570	300
Aluminum	610	NS	820	NS	770	520	480	320	570	440	NS	NS	NS	400	75
Cadmium	2.3	NS	5.0	NS	3.4	2.9	0.9	1.2	4.2	4.6	NS	NS	NS	1.1	0.2
Chromium	220	NS	230	NS	210	150	160	110	190	160	NS	NS	NS	130	100

METALS	DETECTION LEVELS for Industrial Outfalls (µg/L)
Copper	0.005
Lead	0.01
Zinc	0.01
Iron	0.02
Aluminum	0.02
Cadmium	0.01
Chromium	0.02

Note: PWQO excedances at Blackbird Creek discharge signified by underlined values in Table 7.

All measurements were undertaken on unfiltered samples.

NS denotes Not Sampled.

"–" denotes no measurable response above the detection level.

* PWQO for Lead when Alkalinity is > 80 mg/L as Calcium Carbonate.

Bay and along the western shoreline as far as Cody Island.

Over an extended exposure period beyond 96 hours, the aluminum, levels at site 1 may have been lethal to the rainbow trout. The lowest effect concentration (LOEC) for aluminum causing death and deformity to goldfish (Carassius auratus) occurred at 150 ug/L over a 7-day period (Birge, 1978). The pH and water hardness for that study were 7.4 +/- 0.1 and 195 +/- 5.4 mg/L (as $CaCO_3$). The Aluminum, pH and hardness levels during the exposure at site 1 ranged from 330 - 440 ug/L, 7.6 - 7.7 and from 184 - 224 mg/L (as Ca/CO_3), respectively. At the exposure sites beyond site 1, the maximum aluminum level was 140 ug/L, but it occurred for less than 48 hours. Therefore based on long term LOEC of 150 ug Al/L required to produce a toxic effect over a 7-day period, it is unlikely that aluminum levels acting independant of other metals would be expected to have caused an effect beyond site 1. However, sedimentation of Aluminum in a depositional zone in Moberly Bay could adversely affect sensitive benthic biota (Neville, pers. comm.)

In the case of some metals, elevated concentrations above their respective PWQO's may originate as components in the wood feedstock to the mill, which in turn are released as a byproduct of the pulping process (Murphy, pers. comm.).

7. Chloroguaiacols (GC's)

Chloroguaiacols are one of many groups of chlorinated compounds produced in a pulp mill's chlorine-based bleachery (Salkinoga-Salonen et al, 1981) which are readily bioaccumulated by aquatic biota upon discharge to receiving waters (Landner et al,1977; Paasivirta et al, 1983).

Chloroguaiacol detection levels for samples collected throughout the study varied widely between the effluent, controls, site 1 and the other exposure sites; due to interferences by other compounds within those samples. The lowest detection levels (in ug/L) at the exposure sites were as follows:

	Controls	Site 1	Sites 2 - 13
4-chloroguaiacol	100	500	100
4,5-dichloroguaiacol	100	500	100
3,4,5-trichloroguaiacol	200	1000	200
4,5,6-trichloroguaiacol	600	3000	600
Tetrachloroguaiacol	40	200	40
on:	1 of 4 days	all 4 days	2 of 4 days

Tetrachloroguaiacol was the only CG species measured in Jackfish

Bay. It was detected on 3 of 4 days, at levels between 45 - 200 ug/L , while 200 ug/L was the detection level on the 4th day.

Measureable tetraCG concentrations were confined to Moberly Bay during 2 of the 3 days on which it was found. The levels found beyond Moberly Bay were confined to a transect which hugged the western shoreline as far as 3.5 km from the Blackbird Creek disharge, near Victoria Point (Table 8).

Tetrachloroguaiacol was not found in the final effluent from Kimberly Clark or the Blackbird Creek discharge. The detection level for tetrachloroguaiacol in both sets of samples varied between 200 and 400 ug/L.

The 3,4,5- and 4,5,6-trichloroguaiacols have been identified in soft- and hardwood chlorination and caustic extraction effluents by Voss et al (1981) and 2,4-dichloroguaiacol was identified by Paasivirta et al (1983). However, the high detection limits of those chloroguaiacols, which ranged from 500 - 3000 ug/L, precluded the detection and quantification of those compounds in the the Kimberly Clark effluent.

There are currently no PWQO for chloroguaiacols nor are they restricted by the OMOE, Environment Canada or the USEPA.

8. Polyaromatic Hydrocarbons (PAH's)

Sherman (unpublished manuscript) found similar PAH levels in the sediments throughout Jackfish Bay and therefore suggests atmospheric deposition as the source, while Beak (1991) observed decreasing PAH levels in sediments with increasing distance from Moberly Bay.

Phenanthrene is not a primary contaminant in pulp mill effluents but it was found in 16% of the MISA water samples (N=105) collected from all of the kraft mills in Ontario (N=9) during 1990 (MISA, 1992a & 1992b). Phenanthrene was not detected at a level of 0.2 ug/L or greater in either the MISA samples of the Kimberly Clark (Terrace Bay) effluent or in samples of the effluent collected during this study. However, phenanthrene levels of 470 ng/L (day 1) and 520 ng/L (day 3) were measured in both water samples (2 of 2) collected from Moberly Bay at the closest cage site to the Blackbird Creek discharge (ie. site 1).

There is a possible explanation for the measurement of phenanthrene in Moberly Bay but not in the mill effluent or Blackbird Creek discharge samples, if infact, the mill is not the current source. A spill of bunker "C" crude oil from the mill was washed down the Blackbird Creek and into Moberly Bay (Pugh, pers. comm). The only reported oil spill occurred in the late 70's and was estimated to be 2250 - 3600 L (ie. 500 - 800 Imp. gal) in size (Huggard, pers.

Table 8: Chloroguaiacol levels at the fish exposure sites in Jackfish Bay during the period from July 26–30, 1990.

DAY No.	Chloroguaiacol levels (μg/L) at exposure sites															Detection Level (μg/L)
	C1	C2	1	2	3	4	5	6	7	8	9	10	11	12	13	
JULY 26 – DAY1																
4–Chloroguaiacol	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	3000
45–Dichloroguaiacol	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	1000
345–Trichloroguaiacol	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	500
456–Trichloroguaiacol	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	500
Tetrachloroguaiacol	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	200
JULY 27 – DAY2																
4–Chloroguaiacol	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	600–1200
45–Dichloroguaiacol	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	200–1000
345–Trichloroguaiacol	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	100–500
456–Trichloroguaiacol	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	100–500
Tetrachloroguaiacol	–	–	–	–	130	45	–	145	–	135	–	90	–	90	–	40–80
JULY 28 – DAY3																
4–Chloroguaiacol	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	600–3000
45–Dichloroguaiacol	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	200–1000
345–Trichloroguaiacol	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	100–500
456–Trichloroguaiacol	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	100–500
Tetrachloroguaiacol	–	–	–	–	–	70	75	180	–	–	–	–	–	–	–	40–200
JULY 30 – DAY5																
4–Chloroguaiacol	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	600–3000
45–Dichloroguaiacol	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	200–1000
345–Trichloroguaiacol	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	100–500
456–Trichloroguaiacol	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	100–500
Tetrachloroguaiacol	–	–	–	55	–	170	200	100	–	–	–	–	–	–	–	40–200

Note: No samples were collected on July 29 (Day4) due to poor weather conditions.

"–" denotes no measurable response above the detection level.

The detection levels in these samples varied through the study (see Discussion for more details).

comm.). Phenanthrenes have been found to make up 11.6% (by weight) of the constituents in an API reference sample of Bunker "C" crude oil (Pancirov, 1974), and hence its presence in the bay may be due to the remnants of that spill in the sediments of the bay.

There was definite evidence of oil in the sediments in Moberly Bay in 1990 (Hitchin, pers. comm.), at locations between sites 3 and 6, site 7 and a location between sites 2 and 4 of this study. However, those particular sediment samples contained only trace amounts of phenanthrene, pyrene, fluoranthrene, chyrsene and anthracene (Jaagumagi, file). There are also other reports describing the remnants of an oil spill out in Jackfish Bay near Cody Island (Beak, 1988).

Anthracene, which is an isomeric with phenanthrene was found at trace amounts of 3.0 and 4.0 ng/L in the Moberly Bay samples referred to in the previous paragraph. There is currently no PWQO's for anthracene or phenanthrene.

No other PAH was detected in the effluent or receiving water during this study. A list of PAH species analysed in the samples is presented in Appendix F along with their respective detection limits.

9. Phthalate Esters

Daphnia is the most sensitive aquatic organism to phthalate esters (OMOE, 1979) with butylbenzl phthalate (BBP) and di(2-ethylhexyl) phthalate (DEHP) levels as low as 220 and 0.3 ug/L, respectively, causing chronic toxicity. BBP was not detected in the effluent, Blackbird Creek or Moberly Bay during the study. The no-effect level of DEHP was between 5 and 14 ug/L for the early life stages of rainbow trout (Mehrle & Mayer, 1976), and the PWQO's for DEHP, di-n-butylphthalate (DBP) and all other individual phthalates are 0.6 ug/L, 4.0 ug/L and 0.2 ug/L, respectively (OMOE, 1984).

Phthalate esters are used in defoaming agents during the manufacturing of paper and paperboard and as pesticide carriers, with DEHP being the most widely used phthalate in Canada. The highest levels of DBP and DEHP in the Blackbird Creek discharge were 1.0 ug/L and 3.0 ug/L, respectively (Appendix G). Phthalates were not measured in MISA audit samples of pulp and paper mill effluents. Therefore, based on limited data available from this study, it would appear that DBP concentrations at the mouth of Blackbird Creek were in compliance with its PWQO, while BEHP levels exceeded the guideline in the creek as well as at site 1 in Moberly Bay (Appendix G). There were no other phthalate esters detected in the Kimberly Clark effluent Blackbird Creek discharge or Moberly Bay.

10. Chlorobenzenes

Trace amounts of a few chlorinated benzenes and toluenes (3 of 12) were found in the mill effluent and Blackbird Creek on a sporadic basis (Appendix H). More than one chlorobenzene species was measured in only 1 of 9 samples (ie. 5 effluent and 4 creek samples) at any time during the study and 3 of the detectable levels in those samples were for pentachlorobenzene. Such a finding is not unexpected for Lindstrom et al (1981) identified pentachlorobenzene as one of many chlorinated compounds found in spent chlorination and alkali extraction liquors. The pentachlorobenzene concentrations in the effluent (25 ng/L) and Blackbird Creek (10 & 20 ng/L) were below the Ontario's PWQO of 30 ng/L.

The most prevalent CB found in the MISA audit sampling (MISA, 1991a & 1991b) of Kraft mills was 2,4,5-trichlorotoluene (33% of 53 samples). It was found at a level of 40 ng/L in 1 of 9 Kimberly Clark effluent samples collected during this study, however there is currently no PWQO for chlorinated toluenes.

Samples from Jackfish Bay were not analysed for chlorobenzenes.

11. Phenoxy Acid Herbicides

Phenoxy acid herbicides have been found in pulp mill wastes previously (Flood et al, 1989). Among some of the herbicides that contain phenoxy acids as active ingredients are the Tordon 101R "Forestry Herbicide" (Dow) which contains 2,4-dichlorophenoxyacetic acid and silvex, as well as Butyrac 118 (Amchem) which contains 2,4-dichlorophenoxybutyric acid (Gosselin et al, 1984).

On the 5th day of the fish exposure, 2,4-dichlorophenoxybutyric acid (2,4-DB) levels were measured in the Blackbird Creek discharge and at three sites in Moberly Bay, but not in the effluent during any of the preceeding days (Appendix I). There is a 1.5 - 2 day travel time between the mill and Moberly Bay, and based on the fact that phenoxy acids were not found in the effluent, the 2,4 DB did not likely originate from the mill or its wood supply for herbicides are only used in site preparation prior to the planting of seedlings and the resultant wood supply is not harvested until about 40 years later (Gerry Gammond, pers. comm.).

Possible sources of this herbicide may be brush kill spraying along the highway, hydro rights-of-way or the CP rail line. There is a hydro right of way that cuts through the study area. It crosses Moberly Bay near site 1, approximately 0.6 km from 2 of sites at which 2,4-DB was found (DEMR, 1968). Currently, there is no information to confirm that Ontario Hydro uses 2,4-DB as a herbicide to control brush.

12. Mirex

There were indications that Mirex was present in the Kimberly Clark effluent on several occasions. It was found in the effluent on 2 of 8 occasions at concentrations of 10 and 40 ng/L with the proviso that they were considered as trace levels and therefore the results are to be interpreted with caution. A level of 50 ug/L with no provisos was reported in the effluent and Blackbird Creek discharge on study day 5. There is no evidence presented in the literature which states or would suggest that mirex could be found in pulp mill effluents. Furthermore, false positives of mirex have been found in biota samples (Suns, pers. comm.) and therefore these data are considered suspect.

13. Dioxins and Furans

The recovery levels of dioxins and furans measured in this study were low, which in turn produced questions about the reliability of the results and therefore they have not been reported.

CONCLUSIONS

1. The Kimberly Clark mill effluent met all of the toxicity requirements of the 1987 MOE control order.

2. The Kimberly Clark mill effluent met the proposed toxicity criteria for the MISA regulation of industrial discharges.

3. There was a dramatic improvement in dissolved oxygen levels in Jackfish Bay during the 1990 study as opposed to conditions measured in the 1983 study.

4. All of the dissolved oxygen levels measured in the surface waters of Jackfish Bay met the Provincial Water Quality Objective for the protection of aquatic life during the 1990 study.

5. The water quality of Moberly Bay has improved to the point that a significant number of suckers (*Catostomus sp.*) were observed foraging in its uppermost reaches.

6. The internal plant changes instituted over the years and the secondary treatment plant combined to produce improvements in the levels of resin and fatty acids discharged to Jackfish Bay.

7. The results of this study demonstrate that full and adequate treatment of the pulp mill effluent required to reduce its biochemical oxygen demand and acute fish lethality occurred prior to its discharge into Jackfish Bay.

8. Changes undertaken in the bleachery in 1990 (&/or the improved treatment system) appear to have produced significant decreases in chloroform and chlorophenol levels discharged from the mill.

9. The PWQO's were met in Blackbird Creek for all organochlorine compounds and metals measured in this study except di(2-ethylhexyl) phthalate (DEHP), aluminum, iron, chromium and zinc.

10. The PWQO's for aluminum, iron, chromium, zinc and DEHP were not met in Moberly Bay, but were met in Jackfish Bay.

11. Trace amounts of phenoxy acid herbicides were found in the Blackbird Creek discharge and Moberly Bay but not in the pulp mill effluent. Possible sources of this herbicide may be brush kill spraying along the highway, hydro rights-of-way or the CP rail line.

REFERENCES

Beak Consultants Ltd. 1988. Benthic Community Evaluation of Jackfish Bay, Lake Superior - 1969, 1975, 1987. Remedial Action Plan Technical Report Series, Ont. Min. Envir. & Envir. Can., Thunder Bay, Ontario. 220 pp.

Beak Consultants Ltd. 1991. Environmental Impact Assessment of Kimberly Clark Effluent on the Aquatic Environment, Jackfish Bay, Lake Superior - 1991. Draft report. Prepared for Kimberly Clark of Canada Ltd.

B.C. Research. 1979. Biological Characteristics of Pulp Mill Effluents (Part 1). Dept. of Envir., Environmental ProtectionService, Ottawa, Ont., CPAR Report 678-1.

Birge, W.J. 1978. Aquatic Toxicology of Trace Elements of Coal and Fly Ash. In Energy and Environmental Stress in Aquatic Systems. J.H. Thorp and J.W. Gibbons (eds.) Tech. Inform. Service Center, Springfield, Virginia. p. 219-230.

Bonsor, N., N McCubbin and John Sprague. 1988. Kraft Mill Effluents in Ontario. Rerort Prepared For MISA Advisory Comm., Ontario Min. of Envir., 260pp.

Cherwinsky, C. and D. Murray. 1986. Preliminary Investigation of Trace Contaminants in Pulp and Paper Mill Effluents. Ontario Min. of Envir., Wat. Res. Br., Toronto. 136 pp.

Craig, G., K. Flood, J. Lee and M. Thomson. 1983. Protocol to Determine the Acute Lethality of Liquid Effluents to Fish. Ontario Min. of Env., Wat. Res. Br., Rexdale, Ont. 9pp.

DEMR. 1968. Topographical Map of Schreiber, Thunder Bay District, Dept. of Energy, Mines and Resources of Canada, Surveys and Mapping Branch, Map Distribution Office, Ottawa, Reference 42 D/14 E.

Flood, K., D. Hollinger, M. Thomson, W. Wager and W. Banas. 1986. Jackfish Bay: Acute Lethalit and Chlorophenol Bioconcentration in Fish Exposed to a Bleached Kraft Mill Effluent (BKME) Plume. Ontario Ministry of Environment, Wat. Res. Br., Rexdale, Ont. 44 pp.

Flood, K.W., A. Smith, D Hollinger and M. Mueller, 1989. Acute Lethality and Related Contaminants in the Rainy River downstream of Two Boise Cascade Kraft Mill Discharges. Rexdale, Ontario. Ontario Ministry of Environment, Wat. Res. Br., Rexdale, Ont. 65 pp.

Gammond, G., Pesticides Officer, OMOE, Thunder Bay, pers. comm.

German, M. and D. Pugh. 1969. Biological Evaluation of the Pollution Status of Jackfish Bay, Lake Superior. Ontario Ministry of Environment, Thunder Bay, Ontario. 17 pp.

Gosselin, R.E., R.P. Smith and H.C. Hodge. 1984. Clinical Toxicology of Commercial Products - fifth ed. Williams & Wilkens, Baltimore, Md.

Hamilton, J.G. 1987. Survey of Critical Fish Habitat within IJC Designated Areas of Concern, August - November, 1986. B.A.R. Environmental, Guelph, Ontario (for Ont. Min. of Nat. Res., Toronto).

Hitchin, G., Biomonitering Program Technician, OMOE, Rexdale, pers. comm.

Huggard, V., former Environmental Officer for Kimberly Clark, OMOE, Thunder Bay, pers. comm.

IJC. 1978. Great Lakes Water Quality Agreement. Intern. Joint Comm., Windsor, Ontario.

IJC. 1981. Report of the Aquatic Ecosystem Objectives Committee. Great Lakes Science Advisory Board, Intern. Joint Comm., Windsor, Ontario. 127 pp.

Jaagumagi, R., Sediments Scientist, OMOE, Toronto, file.

Jackfish Bay RAP Team. 1991. Jackfish Bay Remedial Action Plan, Stage 1: Environmental Conditions and Problem Definition. September, 1991. 157pp.

Landner, L., K. Linstrom, M. Karisson, J. Nordin and L. Sorenson. 1977. Bioaccumulation in Fish of Chlorinated Phenols from Kraft Mill Bleachery Effluents. Bull. of Envir. Cont. & Toxicology, Vol. 18, No 6, p. 663-673.

Leach, J.M, and A.N. Thakore 1973. Identification of the Constituents of Kraft Pulping Effluent that are Toxic to Juvenile Coho Salmon (Oncorhynchus kisutch). JFRB of Canada, vol 30, no.4, p 479-484.

Leach, J.M, and A.N. Thakore 1977. Compounds Toxic to Fish in Pulp Mill Waste Streams. Prg. Wat. Tech., Vol 9 p 787-798.

Lindstrom K., J. Nordin, F. Osterberg. 1981. In "Advances in the Identification and Analyses of Organic Pollutants in Water", Keith, L.H. (ed); Ann Arbor Science, Ann Arbor, Mich.

Mehrle & Mayer, 1976. dI-2-ethylhexyl phthalate : residue dynamics and biological effects in rainbow trout and fathead minnows. In Proc. 10th Annual Conf. Trace Substances in Environmental

Health. D.D. Hemphill (ed.) Univ of Missouri, Columbia, MI. p. 519-525.

McLeay, D.J. 1987. Aquatic Toxicity of Pulp and Paper Mill Effluents: A Review. Environment Canada, Ottawa. Rep. EPS 4/PF/1. 191pp.

MISA. 1991a. Preliminary Report on the first six months of Process Monitering in the MISA Pulp and Paper Sector (Jan. 1, 1990 to June 30, 1990). Water Resources Branch, Ontario Ministry of the Environment. Toronto, Ontario. PIBS No. 1436. 176pp.

MISA. 1991b. Preliminary Report on the second six months of Process Monitering in the MISA Pulp and Paper Sector (July 1, 1990 to Dec. 31, 1990). Water Resources Branch, Ontario Ministry of the Environment. Toronto, Ontario. PIBS No. 1671. 159pp.

Murphy, J., Environmental Officer Supervisor, OMOE, Thunder Bay, pers. comm.

Neville, C., Vertebrate Toxicology Scientist, OMOE, Rexdale, pers. comm.

OMOE. 1979. Rationale for the Establishment of Ontario's Provincial Water Quality Objectives. Ontario Ministry of the Environment, Toronto, Ontario. 236 pp.

OMOE. 1984. Water Management: Goals, Policies, Objectives and Implementation Procedures of the Ministry of the Environment. Ontario Ministry of the Environment, Toronto, Ontario. 70 pp.

OMOE. 1992a. Acute Lethality Data for Ontario's Pulp and Paper Sector Effluents Covering the Period from Jan., 1990 to June, 1990. Toxicity Unit, Water Resources Br., Ontario Ministry of the Environment, Toronto, Ontario. PIBS No. 1831. 74 pp.

OMOE. 1992b. Acute Lethality Data for Ontario's Pulp and Paper Sector Effluents Covering the Period from July, 1990 to Dec., 1990. Toxicity Unit, Water Resources Br., Ontario Ministry of the Environment, Toronto, Ontario. PIBS No. 1830. 76 pp.

Paasivirta, J., J Sarkka, T. Leskijarvi and A. Roos. 1983. Transportation and Enrichment of Chlorinated Phenolic Compounds in Different Aquatic Food Chains. Chemosphere, Vol. 9, p. 441-456.

Pancirov, R.J., 1974. Compositional data on API reference oils used in biological studies: a No. 2 fuel oil, a Bunker C, Kuwait crude oil and South Louisiana crude oil. American Petroleum Institute. p. 103-113.

Pierce, R.C., S.P Mathur, D.T. Williams and M.J. Boddington. 1980.

Phthalate Esters in the Aquatic Environment. Nat. Research Council of Can., Pub. NRCC No.17583.

Poirier, D., G.F. Westlake and s.g. Abernethy. 1988. Daphnia magna Acute Lethality Toxicity Test Protocol. Ontario Ministry of Environment, Wat. Res. Br., Rexdale, Ont. 25pp.

Pugh, D., Senior Environmental Officer, OMOE, Thunder Bay, pers. comm.

Salkinoja-Salonen, M., M.-L. Saxelin, J. Pere, T. Jaakkola, J. Saarikoski, R. Hakulinen andO. Koistinen. 1981. Analysis of Toxicity and Biogradability of Organochlorine Compounds Released into the Environment in Bleaching of Kraft Pulping. In Advances in the Identification and Analysis of Organic Pollutants in Water, L.H. Keith (ed). Vol. 2, Chapter 56, p. 1131-1162.

Sherman, K.R. 1991. Data Report: Environmental Survey of Jackfish Bay, Lake Superior - 1987, 1988. Ontario Ministry of Environment, Wat. Res. Br., Toronto, Ont. 34pp.

Sherman, K.R. (unpublished manuscript). Report on the Jackfish Bay Environmental Survey, 1987/1988. Ontario Ministry of Environment, Wat. Res. Br., Toronto, Ont.

Stephan, C.E. 1977. Methods for Calculating an LC50. Aquatic Toxicology and Hazard Evaluation ASTM STP 634 F.L. Mayer and J.L. Hamelick (eds). American Society of Testing and Materials, pp. 65-84.

Suns, K., Young Fish Scientist, OMOE, Rexdale, pers. comm.

Taylor, B.R., K.L. Yeager, S.G. Abernethy and G.F. Westlake. 1988. Scientific Criteria Document fpor Development of Provincial Water Quality Objectives and Guidelines - Resin Acids. Ontario Ministry of Environment, Wat. Res. Br., Rexdale, Ont. pp. 54.

USDHHS. 1981. Second Annual Report on Human Carcinogens. Dept. of Health & Human Serv., Public Health Serv., Washington, D.C. National Toxicology Program.

USEPA. 1980. Ambient Water Quality Criteria for Chloroform. Environmental Protection Agency, Criteria & Standards Division, Washington, D.C., EPA-440/5-80-033 (NTIS: PB81-117442) 70pp.

Voss, R.H., J.T. Wearing and A. Wong. 1981. A Novel Gas Chromotagraphic Method for the Analysis of Chlorinated Phenolics in Pulp Mill Effluents. In Advances in the Identification and Analysis of Organic Pollutants in Water, L.H. Keith (ed). Vol. 2, Chapter 53, p. 1059-1095.

APPENDICES

Appendix A: Laboratory bioassay results using Daphnia magna to measure the acute lethality of 24-h composite samples of the Kimberly Clark mill effluent during the period from July 23-28, 1990.

			Daphnia Mortality / Test Solution		
Sample Date	Exposure Day(s)	Bioassay LC50 (%v/v)	Effluent Concentration (%v/v)	Daphnia Mortality (%)	LT50 for 100% Effluent (h)
July 23-24	pre-exp day 1	>100	100 60 30 15 control	8 0 0 0 8	NA
July 24-25	pre-exp day2	>100	100 60 30	8 0 0	NA
July 25-26	1	>100	100 60 30 15 5 control	16 16 8 33 8 8	NA
July 26-27	2	non lethal	100 50	0 0	NA
July 27-28	3	non lethal	100 50	0 0	NA

Note: There is a 1.5 - 2 day travel time between the mill and Blackbird Creek discharge, therefore two of the mill effluent samples were collected 1 and 2 days prior to the fish exposure to give an opportunity to compare the bioassay results at the two sites during the fish exposure period.

NA indicates not applicable.

Appendix B: Laboratory bioassay results using Daphnia magna to measure the acute lethality of 24-h composite samples of the Blackbird Creek discharge during the period from July 25-30, 1990.

Sample Date	Exposure Day(s)	Bioassay LC50 (%v/v)	Daphnia Mortality / Test Solution Creek Concentration (%v/v)	Daphnia Mortality / Test Solution Daphnia Mortality (%)	LT50 for 100% Effluent (h)
July 25-26	1	>100	100	33	NA
			60	25	
			30	58	
			15	16	
			5	41	
			control	0	
July 26-27	2	non lethal	100	0	NA
			60	0	
			30	0	
July 27-28	3	>100	100	0	NA
			60	0	
			30	8	
			15	0	
July 28-29	4	no sample collected	-	-	-
July 29-30	5	non lethal	100	0	NA
			50	0	

Note: NA indicates not applicable.

Appendix C: Concentration of volatile organic compounds found in the final effluent (EFF) of the Kimberly Clark mill and at the Blackbird Creek discharge (BBC) during the period from July 24, 1990 (Pre–Exp Day 1) to July 30, 1990 (Day 5).

COMPOUND	PRE-EXP DAY 1		PRE-EXP DAY 2		DAY 1		DAY 2		DAY 3		DAY 5		June 27/90	July 4/90
	EFF	BBC	EFF	BBC	EFF	BBC	EFF	BBC	EFF	BBC	EFF	BBC	EFF	EFF
1,1-dichloroethylene	- (0.2)		- (0.2)		- (0.2)	- (0.2)	- (0.2)	- (0.2)	- (0.2)	- (0.2)		- (0.2)	- (0.4)	- (0.2)
dichloromethane	- (1.0)		- (1.0)		- (1.0)	- (1.0)	- (1.0)	- (1.0)	- (1.0)	- (1.0)		- (1.0)	- (2.0)	- (1.0)
trans-1,2-dichloroethylene	- (0.1)		- (0.1)		- (0.1)	- (0.1)	- (0.1)	- (0.1)	- (0.1)	- (0.1)		- (0.1)	-	-
1,1-dichloroethane	- (0.1)		- (0.1)		- (0.1)	- (0.1)	- (0.1)	- (0.1)	- (0.1)	- (0.1)		- (0.1)	- (0.2)	- (0.1)
cis-1,2-dichloroethylene	- (0.1)		- (0.1)		- (0.1)	- (0.1)	- (0.1)	- (0.1)	- (0.1)	- (0.1)		- (0.1)	-	-
chloroform	4.0		4.8		5.9	1.0	6.4	0.9	5.2	1.0		0.9	6.1	6.5
1,1,1-trichloroethane	- (0.1)		- (0.1)		- (0.1)	- (0.1)	- (0.1)	- (0.1)	- (0.1)	- (0.1)		- (0.1)	- (0.2)	- (0.1)
1,2-dichloroethane	- (0.1)	N	- (0.1)	N	- (0.1)	- (0.1)	- (0.1)	- (0.1)	- (0.1)	- (0.1)	N	- (0.1)	- (0.2)	- (0.1)
benzene	- (0.1)	O	- (0.1)	O	- (0.1)	- (0.1)	- (0.1)	- (0.1)	- (0.1)	- (0.1)	O	- (0.1)	- (0.2)	- (0.1)
carbon tetrachloride	-	T	-	T	-	-	-	-	-	-	T	-	- (0.1)	-
1,2-dichloropropane	-		-		-	-	-	-	-	-		-	- (0.1)	-
trichloroethylene	-		-		-	-	-	-	-	-		-	- (0.1)	-
bromodichloromethane	-		-		-	-	-	-	-	-		-	- (0.1)	-
toluene	-	S	-	S	-	-	-	-	-	-	S	-	- (0.1)	-
1,1,2-trichloroethane	-	A	-	A	-	-	-	-	-	-	A	-	- (0.1)	-
dibromochloromethane	-	M	-	M	-	-	-	-	-	-	M	-	- (0.1)	-
1,2-dibromoethane	- (0.1)	P	- (0.1)	P	- (0.1)	- (0.1)	- (0.1)	- (0.1)	- (0.1)	- (0.1)	P	- (0.1)	- (0.2)	- (0.1)
tetrachloroethylene	-	L	-	L	-	-	-	-	-	-	L	-	- (0.1)	-
chlorobenzene	-	E	-	E	-	-	-	-	-	-	E	-	- (0.1)	-
ethylbenzene	-	D	-	D	-	-	-	-	-	-	D	-	- (0.1)	-
m/p-xylene	0.2		0.06		0.06	-	-	-	-	-		-	- (0.1)	-
bromoform	-		-		-	-	-	-	-	-		-	- (0.1)	-
o-xylene	0.1		-		-	-	-	-	-	-		-	- (0.1)	-
1,1,2,2-tetrachloroethane	-		-		-	-	-	-	-	-		-	- (0.1)	-
1,3-dichlorobenzene	-		-		-	-	-	-	-	-		-	- (0.1)	-
1,4-dichlorobenzene	-		-		-	-	-	-	-	-		-	- (0.1)	-
1,2-dichlorobenzene	-		-		-	-	-	-	-	-		-	- (0.1)	-

Note: "–" denotes no measurable response above the detection level of 0.05 $\mu g/L$, unless otherwise stated in brackets.

No samples were taken on Day 4 (July 29) due to poor weather conditions.

Appendix D: Chlorophenol concentrations in the Kimberly Clark effluent (EFF) and the Blackbird Creek discharge (BBC) from July 26, 1990 (Pre-Exp Day 1) to July 30, 1990 (Day 5).

CHLOROPHENOL CONCENTRATIONS (ng/L)

CHLOROPHENOL COMPOUNDS	PRE-EXP DAY 1		PRE-EXP DAY 2		DAY 1		DAY 2		DAY 3		DAY 4		DAY 5	
	EFF	BBC	EFF	BBC	EFF	BBC	EFF	BBC	EFF	BBC	EFF	BBC	EFF	BBC
246-Trichlorophenol	80	NS	55	NS	-	-	LA	-	90	-	NS	NS	NS	-
245-Trichlorophenol	-	NS	-	NS	-	-	LA	-	-	-	NS	NS	NS	-
234-Trichlorophenol	-	NS	-	NS	-	-	LA	-	-	-	NS	NS	NS	-
2356-Tetrachlorophenol	-	NS	-	NS	-	-	LA	-	110	-	NS	NS	NS	-
2345-Tetrachlorophenol	-	NS	-	NS	-	-	LA	-	-	-	NS	NS	NS	490
Pentachlorophenol	80	NS	-	NS	-	-	LA	-	-	-	NS	NS	NS	-

CHLOROPHENOLS	DETECTION LEVELS (ng/L)
246-Trichlorophenol	> 50
245-Trichlorophenol	> 50
234-Trichlorophenol	>100
2356-Tetrachlorophenol	> 50
2345-Tetrachlorophenol	> 50
Pentachlorophenol	> 50

Note: LA denotes lab accident, no result.

NS denotes no sample.

"-" denotes no measurable response above the detection level.

Appendix E: Chlorophenol concentrations (ng/L) at fish exposure sites in Jackfish Bay during the period from July 26–30, 1990.

DAY No.	CHLOROPHENOL COMPOUNDS	CHLOROPHENOL CONCENTRATIONS (ng/L) AT SITES														
		C1	C2	1	2	3	4	5	6	7	8	9	10	11	12	13
Day1	246-Trichlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	245-Trichlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	234-Trichlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	2356-Tetrachlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	2345-Tetrachlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Pentachlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Day2	246-Trichlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	245-Trichlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	234-Trichlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	2356-Tetrachlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	2345-Tetrachlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Pentachlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	340	-	-
Day3	246-Trichlorophenol	-	-	-	-	-	-	-	-	-	-	90	-	-	-	-
	245-Trichlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	234-Trichlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	2356-Tetrachlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	2345-Tetrachlorophenol	-	-	-	-	-	325	200	-	-	-	-	-	-	-	-
	Pentachlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Day4	All Compounds	NO SAMPLES COLLECTED														
Day5	246-Trichlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	245-Trichlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	234-Trichlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	2356-Tetrachlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	2345-Tetrachlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Pentachlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Note: " – " denotes no measurable response above the detection level.

The detection level was > 50 ng/L for all chlorophenols except for 2,3,4–Trichlorophenol, which had a detection level of > 100 ng/L.

Appendix F: PAH compounds and related detection levels (μg/L).

PAH Compounds	Detection Levels for Mill Effluent (μg/L)	Detection Levels for Receiving Waters (ng/L)
Naphthalene	0.2	–
Phenanthrene	0.2	1.0
Anthracene	0.2	1.0
Fluoranthene	0.2	20.0
Pyrene	0.2	20.0
Benzo(A)Anthracene	0.2	20.0
Chrysene	0.2	50.0
Dimethyl Benzo(A)Anthracene	–	5.0
Benzo(E)pyrene	–	50.0
Benzo(B)Fluoranthrene	0.2	10.0
Perylene	0.5	10.0
Benzo(K)Fluoranthrene	0.2	1.0
Benzo(A)Pyrene	0.2	5.0
Benzo(G,H,I)Perylene	0.2	20.0
Dibenzo(A,H)Anthracene	0.2	10.0
Indeno(1,2,3-C,D)Pyrene	0.5	20.0
Benzo(B)Chrysene	–	2.0
Coronene	–	10.0
Acenapthylene	0.2	–
Acenaphthene	0.2	–
Fluorene	0.2	–

Note: The effluent and receiving water samples 1) do not have the same detection levels due to the higher concentrations of interfering compounds in the effluent, 2) are not analyzed on the same machine, and 3) in some cases are not analyzed for the same compounds.

Appendix G: Phthalate ester concentrations (μg/L) in the Kimberly Clark mill effluent (EFF), Blackbird Creek discharge (BBC) and fish exposure Site 1 ,from July 24, 1990 (Pre–Exp Day 1) to July 30, 1990 (Day 5).

Day No.	Phthalate Compounds	EFF	BBC	Exp. Site #1
Pre–Exp Day 1	Di–n–butylphthalate (0.2)*	–	NS	NS
	Butylbenzylphthalate (0.5)	–	NS	NS
	Di–n–octylphthalate (0.2)	–	NS	NS
	Di–(2–ethylhexyl)phthalate (1.0)	1.0	NS	NS
Pre–Exp Day 2	Di–n–butylphthalate	–	NS	NS
	Butylbenzylphthalate	–	NS	NS
	Di–n–octylphthalate	–	NS	NS
	Di–(2–ethylhexyl)phthalate	2.0	NS	NS
Day 1	Di–n–butylphthalate	1.2	1.0	1.2
	Butylbenzylphthalate	–	–	–
	Di–n–octylphthalate	–	–	–
	Di–(2–ethylhexyl)phthalate	–	–	1.0
Day 2	Di–n–butylphthalate	1.4	0.8	1.2
	Butylbenzylphthalate	–	–	–
	Di–n–octylphthalate	–	–	–
	Di–(2–ethylhexyl)phthalate	–	3.0	1.0
Day 3	Di–n–butylphthalate	1.0	0.4	–
	Butylbenzylphthalate	–	–	–
	Di–n–octylphthalate	–	–	–
	Di–(2–ethylhexyl)phthalate	1.0	1.0	–
Day 4	All Compounds	NO	SAMPLES	COLLECTED
Day 5	Di–n–butylphthalate	NS	0.8	0.8
	Butylbenzylphthalate	NS	–	–
	Di–n–octylphthalate	NS	–	–
	Di–(2–ethylhexyl)phthalate	NS	–	1.0

Note: "–" denotes no measurable response above the detection level.

* detection levels shown in brackets.

NS signifies not sampled.

All measurable values are considered to be trace amounts and therefore they must be interpreted with caution.

Appendix H: Chlorobenzenes in the final effluent (EFF) of the Kimberly Clark mill and Blackbird Creek (BBC) discharge during the period from July 24, 1990 (Pre-exp Day 1) to July 30, 1990 (Day 5).

CHLOROBENZENE CONCENTRATIONS (ng/L)

CHLOROBENZENE COMPOUNDS	PRE-EXP DAY 1		PRE-EXP DAY 2		DAY 1		DAY 2		DAY 3		DAY 4		DAY 5		DETECTION LEVEL (ng/L)
	EFF	BBC	EFF	BBC	EFF	BBC	EFF	BBC	EFF	BBC	EFF	BBC	EFF	BBC	
135-Trichlorobenzene	–	NS	–	NS	–	–	–	–	–	–	NS	NS	NS	–	2.0
124-Trichlorobenzene	–	NS	–	NS	–	–	–	–	–	–	NS	NS	NS	–	2.0
Hexachlorobutadiene	–	NS	–	NS	–	–	–	–	–	–	NS	NS	NS	–	1.0
123-Trichlorobenzene	–	NS	–	NS	–	–	–	–	–	–	NS	NS	NS	–	1.0
245-Trichlorotoluene	–	NS	–	NS	–	–	–	40	–	–	NS	NS	NS	–	1.0
236-Trichlorotoluene	–	NS	–	NS	–	–	–	–	–	–	NS	NS	NS	–	1.0
1235-Tetrachlorobenzene	–	NS	–	NS	–	–	–	–	–	–	NS	NS	NS	–	1.0
1245-Tetrachlorobenzene	–	NS	–	NS	–	–	–	–	25	–	NS	NS	NS	–	1.0
26a-Trichlorotoluene	–	NS	–	NS	–	–	–	–	–	–	NS	NS	NS	–	1.0
1234-Tetrachlorobenzene	–	NS	–	NS	–	–	–	–	–	–	NS	NS	NS	–	1.0
Pentachlorobenzene	–	NS	–	NS	–	–	25	20	–	10	NS	NS	NS	–	1.0
Hexachlorobenzene	–	NS	–	NS	–	–	–	–	–	–	NS	NS	NS	–	1.0

Note: NS denotes not sampled.

"–" denotes no measurable response above the detection level.

Appendix I: Phenoxy acid concentrations at fish exposure sites in Jackfish Bay during the period of July 26–30, 1990.

DAY No.	PHENOXY ACID COMPOUNDS	PHENOXY ACID CONCENTRATIONS (ng/L) AT SITES														
		C1	C2	1	2	3	4	5	6	7	8	9	10	11	12	13
DAY1	Dicamba	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	24-Dichloropropionic acid (24-DP)	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	24-Dichlorophenoxyacetic acid (24-D)	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	Silvex	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	245-Trichlorophenoxyacetic acid (245-T)	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	24-Dichlorophenoxybutyric acid (24-DB)	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
DAY2	Dicamba	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	24-Dichloropropionic acid (24-DP)	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	24-Dichlorophenoxyacetic acid (24-D)	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	Silvex	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	245-Trichlorophenoxyacetic acid (245-T)	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	24-Dichlorophenoxybutyric acid (24-DB)	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
DAY3	Dicamba	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	24-Dichloropropionic acid (24-DP)	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	24-Dichlorophenoxyacetic acid (24-D)	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	Silvex	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	245-Trichlorophenoxyacetic acid (245-T)	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	24-Dichlorophenoxybutyric acid (24-DB)	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
DAY4	All compounds	NO SAMPLES COLLECTED														
DAY5	Dicamba	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	24-Dichloropropionic acid (24-DP)	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	24-Dichlorophenoxyacetic acid (24-D)	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	Silvex	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	245-Trichlorophenoxyacetic acid (245-T)	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	24-Dichlorophenoxybutyric acid (24-DB)	–	–	–	–	–	250	270	360	–	–	–	–	–	–	–

Note: "–" denotes no measurable response above the detection level.

The detection levels were 100 μg/L for Dicamba, 24–DP and 24–D; 50 ng/L for Silvex and 245–T; 200 ng/L for 24–DB